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# VENEER MODIFICATION WITH FIRE RETARDANT CHEMICALS

**Master´s Programme in Chemical, Biochemical and Materials Engineering**
**Major in Fibre and Polymer Technology**

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**Abstract**

The aim of this work was to investigate the effects of potential fire retardant chemicals on veneer properties. Flammability is a great disadvantage of wood material in construction, but it can be reduced with the use of fire retardant chemicals. Three chemicals were selected for testing: DAP, SS and DES, of which DAP and SS were known to increase the fire resistance of wood, but little was known about their impact on other veneer properties. Veneer modification with DES was attempted for the first time. Birch veneers were impregnated or soak treated for 3 or 24 hours with the chemicals and the WPG values were determined. Distribution of chemicals within the veneer was investigated with SEM-EDX. Thermal properties and combustibility were investigated by TGA and a fire resistance test, where the samples were ignited and the mass loss and the proceeding of combustion was recorded. Fixation of chemical was assessed by leaching tests according to the EN84 standard, and the wettability and glue bond strength of the modified veneers were analysed with contact angle measurements by sessile drop method and ABES.

Based on the TGA and fire resistance tests, DAP shifted the overall pyrolysis pathway of wood to lower temperatures and therefore reduced the combustion. It also improved the glue bond strength in ABES testing and increased the wettability of veneers. In SEM-EDX DAP was found to be located mostly on the veneer surface, with small deposits on the veneer pits. SS also had an impact on how the pyrolysis proceeded and with high WPG values had good fire resistance, although it increased the time of glowing combustion. It reduced the glue bond strength and increased wettability. DES modification showed a slight fire resistance effect and in low temperatures greatly affected how the pyrolysis of the wood samples proceeded. DES was found to be distributed throughout the veneer material in SEM-EDX imaging. In leaching tests most of the chemicals were completely leached out of the wood, only a few SS and DES samples having minor proportions of chemical present after testing.

The results from this study showed that DAP was superior in increasing the fire resistance of wood, although SS also had an adequate performance. The adhesion and wettability characteristics of fire retardant modified veneer remain poorly known, which leaves room for further research. Additionally, the potential of DES as a wood modification agent should be investigated further. The mechanism behind the slight fire resistance effect could be studied more and overall the impact of DES on wood properties should be explored.

**Keywords** Adhesion, Fire retardant chemicals, TGA, Veneer, Wood combustion

**Tekijä** Saara Hautamäki

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**Laitos** Biotuotteiden ja biotekniikan laitos

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**Tiivistelmä**

Tämän työn tarkoituksena oli tutkia ja vertailla potentiaalisten palosuojakemikaalien vaikutuksia viilun ominaisuuksiin. Helppo syttyvyys on puumateriaalin suuri heikkous rakennetuissa ympäristöissä, mutta tätä voidaan vähentää palosuojakemikaaleja käyttämällä. Työssä tutkittavaksi valittiin kolme kemikaalia, DAP, SS ja DES, joista kahdella ensimmäisellä tiedettiin olevan palamista rajoittava vaikutus. Viilun modifiointia DES-kemikaalia hyödyntäen kokeiltiin tiettävästi ensimmäistä kertaa. Koivuviiluja käsiteltiin kullakin kemikaalilla vakuumikyllästyksellä tai 3 tai 24 tunnin liotuskäsittelyllä ja määritettiin kunkin tapauksen WPG-arvot. Kemikaalin jakautumista viilun rakenteissa havainnollistettiin SEM-EDX kuvantamistekniikalla. Viilujen lämpöhajoamis- ja palamisominaisuuksia tutkittiin TGA-tekniikalla ja yksinkertaisella palamistestillä, jossa näytteet sytytettiin kontrolloidusti ja niiden massahäviötä ja palamisen etenemistä tarkasteltiin ajan suhteen. Kemikaalien pysyvyyttä tarkasteltiin EN 84 –standardin mukaisella huuhtelukokeella ja viilujen vettyvyys- ja liimautuvuusominaisuuksia tarkasteltiin kontaktikulmamittauksilla sekä ABES-liimasaumatestillä.

TGA- ja palamistestin tulosten perusteella DAP vaikutti voimakkaimmin puun pyrolyysiin siirtäen sitä matalampiin lämpötiloihin ja täten vähentäen palamista. Se paransi myös liimasauman lujuutta ABES-kokeissa ja kasvatti viilumateriaalin vettymistä. SEM-EDX kuvantamisessa DAP:n havaittiin sijaitsevan enimmäkseen viilumateriaalin pinnassa. SS-käsittely vaikutti myös materiaalin pyrolyysikäyttäytymiseen ja korkeilla WPG-arvoilla se muodosti myös hyvän palosuojan, joskin se samalla lisäsi puun kytemisaikaa. Se myös lisäsi vettymistä, mutta heikensi liimasauman lujuutta. DES-käsittely muodosti lievän palosuojan ja etenkin matalissa lämpötiloissa vaikutti suuresti pyrolyysin etenemiseen. DES:in havaittiin levittäytyneen tasaisesti puumateriaaliin SEM-EDX kuvantamisessa. Huuhtelukokeissa lähes kaikki kemikaalit poistuivat puun rakenteista ja vain muutamissa SS- ja DES-näytteissä oli jäämiä kemikaaleista testaamisen jälkeen.

Tämä työ osoitti, että DAP oli palosuojauksessaan ylivoimainen, joskin myös SS-käsittely ylsi tyydyttäviin tuloksiin. Palosuojakäsitellyn viilun adheesio- ja vettyvyysominaisuudet ovat huonosti tunnettuja ja niitä tulisi tutkia lisää. Lisäksi DES-käsittelyn potentiaalia puun modifioinnissa tulisi selvittää lisää ja sille ominainen palosuojamekanismi tulisi selvittää.

**Avainsanat** ABES, Palosuojakemikaalit, Puun palaminen, TGA, Viilu

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**LIST OF NOMENCLATURE**

| | |
|---|---|
| ABES | Automated bonding evaluation system |
| DAP | Diammonium phosphate |
| DES | Deep eutectic solvent |
| DTG | Differential thermogravimetry |
| EDX | Energy dispersive X-ray detector |
| EMC | Equilibrium moisture content |
| RM | Residual mass |
| SEM | Scanning electron microscopy |
| SS | Sodium silicate |
| TGA | Thermogravimetric analysis |

# 1 INTRODUCTION

## 1.1 Background

Wood is a versatile natural material that has many excellent properties, such as a good strength to weight ratio, pleasing aesthetics and great workability. It is also renewable, which makes it an increasingly important source of material in the modern world, where the traditional supplies of nonrenewable resources are steadily depleting. However, wood as a material also has a number of disadvantages. Especially in built environments its sensitivity to moisture and flammability are of great concern. (Hill, 2006, p.19-20; Rowell, 2013, p.3-5)

The flammability of wood can be altered with the utilization of fire retardant chemicals. Research on the subject has a long history and several approaches have been presented. An ideal fire retardant should not only inhibit the combustion of the material effectively, but also be chemically stable and resistant to moisture at normal service conditions, have no effect on the strength properties or aesthetics of the protected material and be easy to apply and economical so that it would be feasible in the industrial scale. Regardless of the great number of products available in the market, only a few of them fulfill these requirements. Additionally, the negative environmental effects of the treatment should be minimized. For example, halogenated compounds were extensively applied as fire retardants for cellulosic materials for over four decades, until they were found toxic and harmful to the environment in the 1990's. There is a growing demand for efficient and sustainable fire retardants. (Kozlowski & Wladyka-Przybylak, 2000; Sharma *et al.*, 2015)

Even though the components of most fire retardant chemicals available on the market have been known for a long time, only limited information is available on their effects on adhesion and other veneer properties. Most of the recent study has been focused on the development of more durable and leach resistant systems. To achieve this, different additives for fire retardant chemicals have been explored with

the intent that they would react with the components of wood and become an inherent part of the material. (Sharma *et al.*, 2015)

## 1.2 Objectives

The objective of this thesis was to investigate and compare the effects of three potential fire retardant chemicals on veneer properties, the focus being on thermal behavior and adhesion. To achieve this objective, the modified veneers were analyzed in several way. Thermal properties and combustibility were investigated by thermogravimetric analysis (TGA) and a simple fire resistance test, where the samples were ignited and the mass loss and flaming and glowing combustion times were recorded. Fixation of chemical was assessed by leaching tests according to the EN84 standard, and the wettability and glue bond strength of the modified veneers were analyzed by contact angle measurements using the sessile drop method and by automated bonding evaluation system (ABES). Additionally, distribution of the fire retardant chemicals in the veneers was investigated by scanning electron microscopy (SEM) combined with chemical compound analysis.

This work is divided in two parts. It starts with a literature review, which is followed by the experimental part. The aim of the literary review was to give an introduction to the chemical processes taking place during wood combustion, how these processes can be altered with fire retardant chemicals and finally on the effects of fire retardant chemicals on veneer adhesion. The experimental part consists of a methodology chapter, followed by results and discussion.

# 2 COMBUSTION OF WOOD

Combustion of wood is a complex series of chemical reactions and physical transformations. Lignocellulosic materials do not burn directly, but first decompose (i.e. pyrolyze) under the influence of heat into carbon-rich and highly reactive char and tarry and volatile compounds. In appropriate conditions, these products may ignite and their heat of combustion maintains the pyrolysis and combustion reactions. Wood is a heterogeneous material consisting of four different components – cellulose, hemicellulose, lignin and a minor proportion of extractives – and even though there are differences in the thermal decomposition between the components, the overall burning of wood is the sum of the behavior of its constituents. (Alén *et al.,* 1996; Browne, 1959; Rowell, 2013 p.127-129)

## 2.1 Thermal degradation of cellulose and hemicelluloses

Cellulose, presented in Figure 1, is the main component of wood by weight and therefore dominates the combustion reaction chemistry. It consists of joined glucose monomer units and has a strong tendency to form crystalline structures due to its chemical constitution and spatial conformation. Hydroxyl groups on the glucose monomer are responsible for the hydrophilic nature and high mechanical stability of the polymer. Together with hemicelluloses, cellulose decomposes mainly to volatile gaseous products under the influence of heat and together they are responsible for the type of wood combustion that produces an observable flame. (Shafizadeh & Fu, 1973, p.113-122; Klemm *et al.*, 1998, p.15; Hill, 2006, p.25)

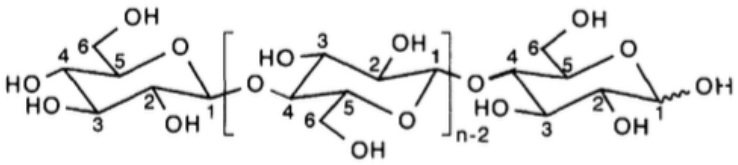



**Figure 1.** Structure of cellulose polysaccharide skeleton (Klemm *et al.*, 1998, p.11).

Because of its crystalline structure, cellulose has a moderate thermal stability. Thermal degradation of cellulose is a complex process, consisting of a large number of consecutive and parallel reactions. It can proceed through two different reaction

routes, depending on the ambient temperature. The first route takes place in temperatures lower than 200 °C, when cellulose undergoes dehydration, in which water is split off along the polymer chain. This causes occasional chain cleavage, but the structure is mostly maintained uncut. At approximately 200 °C the second reaction route prevails and actual thermal decomposition begins. Gaseous products are released at a slow rate but most of the polysaccharide chain stays intact until up to 250 °C. Above this temperature high amounts of carboxyl, carbonyl and aromatic groups are formed. These groups further accelerate the chain splitting: the cellulose molecule is in highly flexible and active state and readily decomposes into products of smaller molecular weight, such as levoglucosan, which is considered to be the main precursor in the formation of flammable volatiles tarry products (Price & Horrocks, 2013 p. 46). Rapid decomposition takes place at 260-320 °C, during which further dehydration takes place and most of the volatiles (i.e. CO and $CH_4$) are formed. When these highly flammable substances mix with oxygen and are provided enough heat to reach their ignition temperature, sudden exothermic flaming combustion occurs. This in turn transfers even more heat back to the substrate, increasing the rate of the pyrolysis reactions and the release of volatile substances. Therefore, the combustion of cellulosic material can be considered a cyclic chain of reactions. Finally above 320 °C is a highly crosslinked carbon skeleton, i.e. char. (Klemm, 1998 p.107-115; Browne 1959; Rowell 2013, p. 129-136)

An example of hemicellulose structure is presented in Figure 2. Hemicellulose polymers are composed of a number of structurally different sugar units, depending on the wood species. Hardwood hemicelluloses are mainly composed of xylan, while softwood contain the highest amount of mannan polysaccharides. Their structure is mainly amorphous with only a very small crystalline region, which means that they contain the largest proportion of accessible hydroxyl groups, have a higher reactivity, and are thermally less stable than cellulose or lignin. Thermal decomposition of hemicelluloses begins at approximately 225 °C and it is almost completely degraded by 325 °C. It yields no levoglucosan or other tarry substances in degradation but evolves more incombustible gaseous products than cellulose – mainly $CO_2$, CO and formic and acetic acids. (Browne, 1959; Hill, 2006, p.26; Chen 2014, p.26-45; Rowell, 2013, p.132-134)

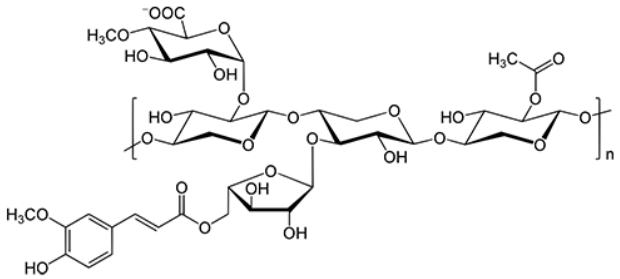


**Figure 2.** An example of hemicellulose structure (Rowell, 2013).

## 2.2 Thermal degradation of lignin

Lignin is an amorphous, randomly cross-linked macromolecule and thermally more stable than cellulose and hemicellulose. Due to its random structure, lignin does not decompose to one major reaction product, such as cellulose to levoglucosan, but rather to an array of different aromatic products and char (Browne 1959). The thermal decomposition of lignin slowly starts at approximately 200 °C, but the polymer remains largely non-degraded until a temperature of 375 °C, at which the majority of the carbohydrate polymers have already decomposed. It decomposes over a broad temperature range, because of the various functional groups in its structure with different thermal stabilities. Lignin gives a notably higher char yield than other components in wood and has a higher heat of combustion, meaning that it releases less heat in combustion. Additionally, the majority of the gaseous products from thermal degradation of lignin are released as incombustible $CO_2$ and therefore it does not contribute to flaming combustion as much as cellulose and hemicelluloses. (Brebu & Vasile, 2010; Rowell, 2013 pp. 134-135)

## 2.3 Reaction-to-fire parameters

Flammability is often considered to be the biggest disadvantage of wood products, thus the use of wood materials in construction is strictly regulated. In practice the term 'flammability' refers to many reaction-to-fire parameters at the same time: ease of ignition, rate of flame spread, critical heat flux, smoke formation and heat release rate are all important aspects in evaluating the fire performance of a material. They can be determined through a set of three standardized test methods: single burning item test (SBI-EN-13823, 2017), small flame test (EN-ISO-11925, 2017) and radiant panel test (SFS-EN-ISO-9239-1, 2002) (Östman & Mikkola, 2006; Östman &

Tsantaridis, 2000). However, these tests mainly provide information about life-size products, such as panels and claddings. On laboratory scale, thermal behavior of materials can be studied in several ways, most commonly by thermogravimetric analysis (TGA) that records the percent weight loss of the sample as a function of time and temperature. It provides information on changes in pyrolysis behavior and potential delay of ignition of fire retardant modified wood. (Rowell, 2013 p.128; Kozlowski & Wladyka-Przybylak, 2000 p.308; Lowden & Hull, 2013)

Fire performance of all building construction elements is classified in the EU area by the Euroclass system, which is based on a set of European standards and specified test methods. This means that the measurements of the reaction-to-fire parameters have to meet a certain defined level: for example, in the standard SFS-EN 13501-1 it is defined that the fire growth rate cannot exceed 120 W/s in order for it to achieve a satisfactory classification. All products on the European market have to be tested according to the Euroclass system to get the mandatory CE-mark. The classification runs from A to F, A1 and A2 being the highest classes and standing for practically non-combustible materials. Untreated wood often falls to the C-class, but fire retardant treated wood may achieve the third highest B-classification, which is sufficient for use in most building environments, excluding only escape routes. (Östman & Tsantaridis, 2000; Östman & Mikkola, 2006)

# 3 IMPROVING THE FIRE RETARDANCY OF WOOD

## 3.1 Fire retardation mechanisms

Several chemical mechanisms exist for fire retardation in lignocellulosic materials, which can take place in different phases of the combustion reaction cycle and aim to change the pyrolysis in favorable direction (Browne 1959). Three major modes of action are known, presented in Figure 3.

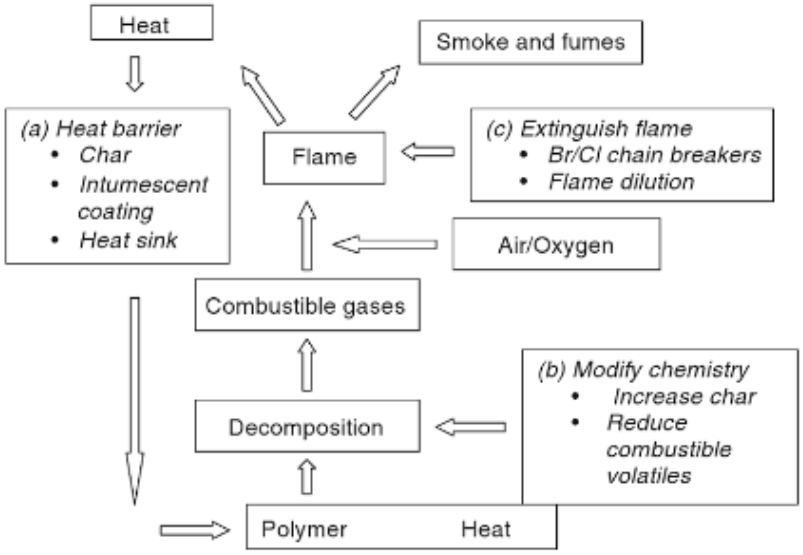



**Figure 3.** Scheme of fire retardation mechanisms and their roles in the combustion reaction cycle. (Price & Horrocks, 2010)

Formation of a heat barrier may prevent the ignition from taking place. Fire retardants working in this mechanism either form a protective barrier around the substrate or provide a heat sink effect, in which the heat is prevented from returning to the wood or removed. Char formation is a good example of a heat barrier effect. The char layer has a thermal conductivity several times lower than wood (Kozlowski & Wladyka-Przybylak, 2000 p.300) and therefore it forms an effective insulating barrier and blocks the heat flow to the wood. Intumescent coatings work in the same manner as they swell under the influence of heat, protecting the material beneath. The second fire retardation mechanism aims at modifying the combustion chemistry by promoting char formation and reducing the amount of volatile products formed in the pyrolysis reactions. Many fire retardants for lignocellulosic materials work by this mechanism by promoting the char formation at lower temperatures than in untreated wood and thus reduce the amount of pyrolysis reactions and volatile products. The third type of flame retardants are based on the flame extinguish mechanism, which takes place in the vapor phase when the volatile products have already ignited. This can be achieved by using bromine- or chloride-containing compounds that terminate the free radical reactions that are essential for the combustion cycle, or by chemicals that release water upon heating. (Price & Horrocks, 2013 p.46; Kozlowski & Wladyka-Przybylak, 2000 p.300-302)

## 3.2 Fire retardant chemicals

The progress in the development of new fire retardant chemicals is relatively slow, especially in the field of wood technology. Most of the research on fire retardants is focused on the protection of polymeric products (Kozlowski & Wladyka-Przybylak, 2000, p. 297). Although manufacturers of commercial products do not give full insight into their fire retardant formulations, the most common chemicals already have a long history of use. They include those based on silica, boron and boric acid, phosphorous, nitrogen and their synergistic combinations (Östman & Tsantaridis, 2000; Lowden & Hull, 2013). However, the use of boric acid is likely to be reduced. In 2008 it was classified as toxic chemical for reproduction and in 2010 it was authorized as a potential substance of a very high concern under REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulations in the EU area (Morgan & Wilkie, 2014 p.201-203; Sharma *et al.*, 2015; Lowden & Hull, 2013). In this work, the selection was narrowed down to three potential chemicals: diammonium phosphate, sodium silicate and a urea-containing deep eutectic solvent.

### *3.2.1 Phosphorous and nitrogen based compounds*

Phosphorous-based chemicals are one of the oldest and largest classes of fire retardants and a variety of formulations has been researched. Their mode of action is a combination of heat barrier formation and flame quenching: under the influence of heat, phosphoric compounds form phosphoric acid in a solid form. This results in charring of the wood material via dehydration reactions, which in turn inhibits the release of flammable gases from cellulose fibers (Klemm, 1998 p.116) and thus prevents the continuation of the combustion cycle. Most of the phosphorous remains in the char residue after combustion (Horrocks, 1996). Additionally, as the phosphoric acid condensates, some water is released. This is an endothermic reaction, which cools down the wood and provides an additional heat sink effect. In wood products, phosphoric compounds are typically used in an inorganic form, which affects more the char formation rather than the volatile gas inhibition. They are water soluble but can be cured with the use of cross-liking agents. (Lowden & Hull, 2013; Morgan & Wilkie, 2014 p.18-22; Sharma *et al.*, 2015)

Nitrogen based chemicals are another widely used class of fire retardants and they are gaining more popularity due to their lack of environmentally harmful effects, such

as release of dioxins or excessive smoke formation. They modify the combustion chemistry by inhibiting the formation of flammable gases and acting as flame dilutors through a release of nitrogen-containing compounds. Char formation also occurs through decomposition of secondary reaction products, although this effect is somewhat small. (Lowden & Hull, 2013; Morgan & Wilkie, 2014, p.146; Sharma *et al.*, 2015)

Phosphorous and nitrogen compounds are not commonly used alone in fire retardants, but as a combination of the two. Together they present effective synergism in cellulosic materials, which enhances the fire performance of the two individual components. The most important examples of phosphorous-nitrogen containing fire retardants are ammonium polyphosphate (APP) and mono- and diammonium phosphate (MAP and DAP), which are all inorganic salts. When exposed to heat, they decompose to ammonia and phosphoric acid. Phosphoric acid releases water as aforementioned and ammonia together with water dilutes the volatile pyrolysis gases. However, the release of acid during service may induce hydrolysis, which can cause premature failure of the wood material (Vick, 1994). Other examples of common P-N synergism include various semi-organic amine and melamine salts of phosphoric acids, which are mostly used for topical surface treatments. (Lowden & Hull, 2013; Morgan & Wilkie, 2014 p.18-22; Sharma *et al.*, 2015)

### *3.2.3 Silicate based compounds*

The most explored form of silicon-based flame retardants for wood are probably those based on silicon dioxides, also known as silicates. They are typically introduced to wood in an alkali form, the most common example being sodium silicate (SS; $Na_2SiO_3$), which is also known as water glass. SS and other silicates are widely employed as additives (e.g. glue extender, detergents, gel-forming agents) in a variety of chemical products. In fire retardant formulations, SS functions by forming a heat barrier of accumulating inorganic silica residues on the wood surface, when sufficient heat and oxygen are provided. This residue functions as an insulating, porous barrier that prevents the release of the volatile pyrolysis products and also reduces the amount of heat that is transferred back to the wood. SS can also be incorporated to phosphorous-nitrogen fire retardant systems, where it can offer even more thermal

stability to their synergism. (Mai & Militz, 2004; Lowden & Hull, 2013; Morgan & Wilkie, 2014 p.172-177)

### *3.2.3 Deep eutectic solvents*

Deep eutectic solvents (DES) are a relatively new class of chemicals consisting of Lewis or Bronsted acids and bases, which can contain a variety of anionic or cationic species. They exhibit a lower melting point compared to either of their components on their own or in any other form of mixture, a phenomenon known as eutectic. Four main classes of DES exist, depending on the complexing agent used in their formulation. Most of them are based on a quarternary ammonium salt, such as choline chloride, combined with either a metal chloride or a hydrogen bond donor. The most common DES system is the combination of choline chloride and urea, presented in Figure 4.

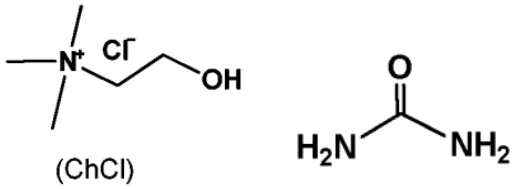



**Figure 4.** Structural formulas of choline chloride and urea. Choline chloride is a quartenary ammonium salt and urea functions as a hydrogen bond donor. (Zhang *et al.*, 2012)

The eutectic effect of this combination takes place when the molar ratio of urea and choline chloride is 2:1. The freezing point of the eutectic mixture is 12 °C, which is significantly lower from that of the individual components (302 °C for choline chloride and 133 °C for urea). (Abbott *et al.*, 2003; Smith *et al.*, 2014) Choline chloride and urea associate with each other and other through hydrogen bond interactions. Especially the quarternary salt component is also able to attach itself to the accessible hydroxyl groups of cellulose and hemicelluloses. DES can function reagents in processes including cellulose or other polysaccharides. They have also been found to be able to dissolve cellulose, although the solubility has been only in minor quantities and the crystallinity remained largely unchanged (Zhang *et al.*, 2012; Tenhunen *et al.*, 2016). DES with different hydrogen bond donors than urea have also been applied in lignin extraction from wood biomass, where DES is able to act as a catalyst in the

bond cleavage. (Abbott *et al*., 2003; Abbott *et al*., 2006; Zhu *et al.*, 2006; Alvarez-Vasco *et al*., 2016)

To date, the potential of DES as a fire retardant has not been studied, as it is overall a fairly novel chemical in wood technology and so far has not been utilized in modification of solid wood. Urea has been explored as a component in fire retardant resin systems, especially in particleboard products, and it is also a common agent intumescent coatings (Syska, 1969; Camino *et al.*, 1989; Rowell, 2013 p.147). Combination of these two may be worth studying, as choline chloride and urea are both nontoxic and biodegradable. Choline chloride is also readily available, because it is commonly used as a nutritional additive in chicken feed and produced on megaton scale every year (Gultom *et al*, 2001; Smith *et al.*, 2014).

## 3.3 Leaching

The problem with several fire retardant chemicals is their lack of fixation within the wood. Wood is often exposed to moist service conditions, which may lead to leaching of the chemical if it is water soluble. This in turn may lead to a release of potentially harmful chemicals to the environment and loss in fire performance over time. It has been reported that for some treatments a field exposure of only one year can reduce the fire retardance potential to the level of untreated samples (Östman & Tsantaridis, 2016). Even at moderate indoor humidity, moisture may lead to problems associated with the hygroscopicity of the fire retardant chemicals, such as salt crystallization on the wood surface, migration of the chemicals within the wood or a higher moisture content of the modified wood product, which is common for inorganic salt-based formulations, such as DAP. Most of the commercial fire retardants are water-based so these issues should be addressed. (Östman & Tsantaridis, 2000; Östman *et al.,* 2001; Tsantaridis *et al.,* 2006) Some organic water-insoluble fire retardants have been developed. These include those based on resins that are polymerized after impregnation to the wood, such as urea and melamine based systems, and polymers that are attached directly to cellulose. However, even resin-based systems have demonstrated some leaching and they are also somewhat costly and more difficult to manufacture. (Östman *et al.*, 2001; Rowell, 2013, p. 147)

Leaching of components from wood is affected by several chemical and physical factors, such as absorption, temperature and permeability of the wood material, but the most important aspect being fixation of the chemical itself (Sloot *et al.*, 1997, p. 214). A number of standard protocols have been developed for leaching measurements on a laboratory scale. Harmonization towards a single protocol has been attempted and as a result a modification of standard EN 84:1997 "Wood preservatives. Accelerated ageing of treated wood prior to biological testing. Leaching procedure" has been found suitable for most conditions. It involves a complete water impregnation stage and therefore it is considered as one of the most severe leaching measurement protocols. For fire retardant modified wood products, total leach resistance with water soaking is seldom needed, but rather the ability to demonstrate durability in humid conditions, such as outdoor exposure and adequate resistance to rainfall. This can be best evaluated with field tests, but they are very time and material consuming. Laboratory standard protocols are therefore a valid approach to measure the relative performance of a treatment, but prediction of actual performance of wood products in service should be done cautiously. (Hingston *et al*., 1999; Östman *et al*., 2001)

## 3.4 Incorporation of fire retardant chemicals to wood material

Several methods exist for lowering the flammability of plywood by flame retardants: coating by protective materials, incorporation of fire retardant chemicals to the glue or chemical impregnation of individual veneers or pressed plywood. (Black, 1958; Grexa *et al.*, 1999)

Coatings, such as protective aluminum foils and special lacquers and paints, are particularly effective in reducing the flammability of wood. They prevent the contact between the wood substrate and the source of ignition and can produce practically incombustible products. However, they also conceal some of the positive aspects of wood, such as moisture buffering qualities and pleasing aesthetics. (White, 1984; Tsantaridis *et al.*, 2006) Mixing fire retardants to the glue can provide some fire protection to plywood products. This could potentially prevent hazardous veneer delamination during combustion or charring. However, addition fire retardant components only to the glue mixture is typically not as effective as modification the

surface veneers. If there are no fire retardant chemicals in the immediate presence of the wood substrate in the plywood surface, ignition cannot be prevented. Some glue and therefore the added fire retardant components are likely to penetrate the wood material during hot pressing, but the veneers would have to be extremely thin for the chemicals to flow to the surface. In a large comparative study by Tsantaridis *et al.* (2006) the overall fire performance of glue-modified plywood was found insufficient to fulfill the Euroclass standards. (Selbo, 1959; Su *et al.,* 1998) Additionally, changes in the glue composition may lead to weakened glue bonds, as is discussed in Chapter 4.1.

Impregnation is the most common method of incorporating fire retardant chemicals to veneers and veneer products. Compared to coatings or special glues, impregnation treatments usually render more durable and leach resistant results. The weak leach resistance of some fire retardant chemicals can be improved with the use of precipitating agents or pre-treatments, so impregnation treatments are usually carried out as multi-step processes. Typically in the first step, the impregnant is diffused to the wood material. The aim is to achieve a full cell wall penetration and therefore sufficient time should be allowed for the chemical to spread throughout the intracellular spaces in the material. This is usually achieved with the aid of applied vacuum or pressure and temperature. With a subsequent treatment the impregnant is rendered insoluble. Some cross-linking may occur between the reactant and the cell wall polymers, but the stability of impregnation treatments are mainly based on the phenomenon that the impregnant is locked in the cell wall; 'trapped' in the free space that it has invaded. Additional chemical bonding may occur between the reactant and the cell wall polymers but this is not a primary requirement. (Hill, 2006 p. 149-150; Kozlowski & Wladyka-Przybylak, 2000 p. 311)

The two-step process is especially common with silicate modifications, where impregnation with silicate solution is followed by infiltration with a metal salt solution. The salt precipitates the silicate within the wood structure, replacing the ionic components. Some of the unreacted salts remain in the cell lumen, which may increase the hydroscopicity of the wood material. However, multi-step applications are expensive and time-consuming in the industrial scale, as the wood needs to be dried between the two steps. There have been attempts to resolve this problem by

utilizing boric acid or an organic acid as an insolubilization agent, mixing them to the reagent solution so that they would promote the polymerization of the sodium silicate inside the wood upon drying. Another approach is to dry the silicate treated wood in high temperatures to render the chemical insoluble. Commercial products such as Organowood™ often use the combination of the two approaches in impregnation treatments. (Mai & Militz, 2004; Pereyra & Giudice, 2009; Hellberg & Öhrn, 2012)

Another option is to chemically modify the wood, which Hill (2006, p.22) defines as "the reaction of a chemical reagent with the wood polymeric constituents, resulting in the formation of a covalent bond between the reagent and the wood substrate". This means that a chemical reacts with the hydroxyl (OH) groups present in the wood cell wall components, especially in cellulose and hemicellulose. The OH groups are responsible for many of the interactions of wood and its environment, especially the moisture behavior of the material. To ensure an effective chemical modification, there should be as many interactions between the reagent and the OH groups as possible. However, not all of the OH groups are accessible: especially the groups associated with the crystalline regions of the cellulose polymers are difficult to react with as the chemical reagents cannot penetrate through them. Fire resistant wood with increased leach resistance could potentially be achieved if the fire retardant components react directly with the OH groups of the cell wall polymers. This has been attempted by the use of enzymes combined with a range of functional groups, but further research is still needed. ("Innofirewood database," n.d.)(Kozlowski & Wladyka-Przybylak 2000, p.311)(Hill, 2006 p.22-29; Tsantaridis *et al.*, 2006)

The reaction-to-fire performance of fire retardant treated wood correlates with the retention levels of the chemical, which refers to the ability of the wood to absorb and continue to hold a substance. With higher retention levels the treatment also maintains the fire performance over a longer period of time, although in some cases higher retention levels may lead to weakened moisture resistance of the wood material. The optimization of fire retardant content is therefore important not only from the economical perspective, but also to prevent an increased risk of hydroscopic problems during the service life of the product. (Chuang & Wang, 2002; Östman & Tsantaridis, 2016) The amount of chemical content may also be reported as the

weight percentage gain (WPG), which is a simple measure for chemical uptake of wood. However, WPG provides no proof of actual chemical bonding between the wood and the reactant. It does not give any information about the distribution of the chemical, which may be present in the cell wall, the lumen or both. The chemical may be able to polymerize and be locked in the wood structure, preventing any leaching, but in these cases a weight gain is still not an indicator of the existence of a chemical bond. Only weight gain accompanied with wood material swelling indicates that the chemical may have penetrated the cell wall. (Hill, 2006, p. 44) To obtain specific information about the spatial distribution of the chemical, other methods are needed, such as SEM combined with compound analysis.

# 4 EFFECTS OF FIRE RETARDANT TREATMENTS ON VENEER ADHESION

Modification with fire retardant chemicals is known to affect the wood properties in several ways. For example, reduction in mechanical properties, increased surface roughness and poor workability have been reported as common consequences of fire retardant treatments. (Ayrilmis *et al.*, 2006; Forest Service & Products Laboratory, 2010; LeVan & Winandy, 2007) In this thesis, the focus in on the study of adhesion of fire retardant modified veneers, which is an important factor in plywood production.

## 4.1 Adhesion on wood surfaces

Wood adhesion is affected by both mechanical and chemical factors that determine the ability of the adhesive to hold together two different surfaces. For mechanical interlocking to take place, the glue has to fill the porous wood material effectively. Adequate interlocking occurs when the glue penetrates the damaged surface layer and reaches sound wood beyond the immediate surface, reaching from two to six cell layers deep. The best results are achieved when the glue further penetrates into the cellular microstructure itself and thus maximizes the surface contact area between the glue and the wood structure. (Forest Service & Products Laboratory, 2010)

The adhesive bond forms once the glue solidifies. Phenol formaldehyde, which is the most common type of plywood adhesive used in Finland, is an example of a thermosetting adhesive. It undergoes irreversible condensation reactions when cured and does not soften or flow again upon reheating. (Finnish Forest Industries Federation, 2002, p. 8)

It is difficult to distinguish the actual chemical effects of fire retardant chemicals on the formaldehyde glue bond formation because of the complexity of the polymerization reaction and also the variability of the glue composition (Black, 1958). However, some of the most common mechanisms are well known. Modification with fire retardant chemicals may cause disturbance with the adhesion of wood surfaces especially in coating systems, because the chemicals interfere with the direct glue contact. This is likely to occur especially with silicate-based systems, as they tend to form a protective film on the wood material (Lowden & Hull, 2013). Fire retardants containing inorganic salts are also known to release acid compounds in elevated temperature and moisture conditions, which are present in the hot-press curing. For example, the effectiveness of DAP as a fire retardant chemical is based on its ability to release phosphoric acid and ammonia in elevated temperatures. Phosphoric acid and ammonia prevent the curing of phenolic resins, which are generally alkaline substances. This may be overcome by an alkaline surface treatment of veneers before bonding, which would add an unwanted extra step in the plywood production process. Changes in the hydroscopicity of wood material, which is a common side effect of many fire retardant chemicals, also affects the glue bond formation, because water is a common carrier agent for most adhesives. (Sernek *et al.*, 2002; Forest Service & Products Laboratory, 2010)

### *4.1.1 Determination of adhesion with ABES method*

ABES (*automated bonding evaluation system*) is a laboratory scale method for assessing glue line tensile strength of plywood. The device can be used for testing small samples, which are glued together so that the resin curing takes place in controlled conditions. With ABES, the most important adhesion parameters, such as press time, temperature and compression can be controlled and optimized and the glue line can either be tested immediately after the pressing or later. However, ABES parameters do not translate to ready industrial scale parameters, but rather give

information about the glue line behavior and sensitivity of the adhesive system to different variables in laboratory scale samples. The results can be used for predicting plywood glue bond strength of life-size panels with very little material. When the sample dimensions are small, uniform quality of samples can be ensured and the effect of lathe checks can be minimized. (Humphrey, 1993; Martins *et al.* 2013, p. 106)

## 4.2 Wettability of wood surfaces

Wettability is the ability of a solid surface to hold contact with a liquid. It defines how fast the liquid can wet and spread on the surface or if the surface will repel it, which can be assessed with contact angle analysis. Contact angle can be measured in several ways, but the simplest technique is the sessile drop method, in which the angle formed between the solid and the line tangent to the droplet at the contact point with the solid is calculated as demonstrated in Figure 5 (Sernek *et al.*, 2002).

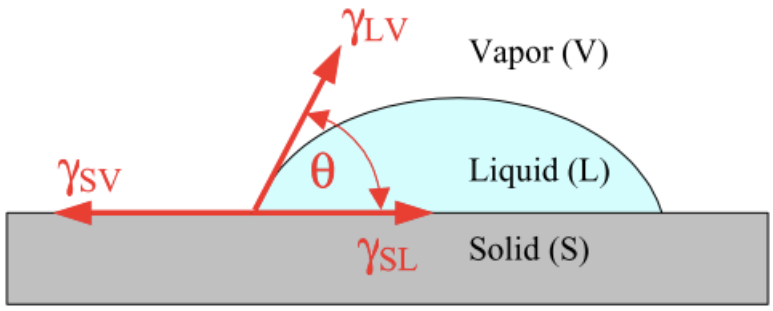



**Figure 5.** Contact angle and interfacial surface tensions at equilibrium (Sernek *et al.*, 2002, p. 25).

Wettability is crucial for excellent adhesion performance, as the adhesive has to spread on the wood surface, flow and penetrate the wood cells to form contact on a molecular level. However, if the wettability is too great and the adhesive is absorbed by the veneer surface too fast, the glue bond formation is again disturbed. Wettability often correlates with adhesion but the real glue bond quality can be only partially predicted by wettability analysis. Contact angle measurement is a useful index in evaluating adhesion, but mechanical testing is the only method for obtaining reliable information about adhesion between wood and glue bond line. (Sernek *et al.*, 2002; Forest Service & Products Laboratory, 2010;)

Wood is a non-ideal and porous material, so the contact angle changes over time as the liquid interacts with the wood surface. This wetting process of wood can be divided to three consecutive phases. At the first stage immediately after initial contact with wood surface, the droplet diameter increases, which results in a rapid decrease in the contact angle value. During the second stage all the pores and irregularities of the surface are completely filled with liquid. The droplet diameter remains nearly constant, but the height of the droplet decreases and therefore the contact angle is slowly reduced. In the final stage the droplet is completely absorbed by the wood surface due to capillary forces. (Liptáková & Kúdela, 1994; Mohammed-Ziegler *et al.*, 2003)

# 5 MATERIALS AND METHODS

## 5.1 Wood material information

The wood material used was 0.8 mm thick rotary cut silver birch (*Betula Pendula*) veneer, felled in Vihti in December 2014. The peeling was performed in January 2015 with an industrial scale lathe (model 3HV66, Raute Oyj), before which the logs were soaked in 70 °C water for 48 hours. Veneers with a high soak temperature were used to ensure a uniform quality of veneers and also to minimize the amount of defects and cracks.

## 5.2 Treatment with fire retardant chemicals

The veneers were cut to dimensions of 116 x 112.5 $mm^2$ and modified with three different chemicals: SS (Merck, 60-w% extra pure aqueous solution), DAP (Merck, ≥99%) and a DES of choline chloride-urea mixture. The DES was prepared by mixing choline chloride and urea (both from Sigma-Aldrich, ≥98%) in a molar ratio of 1:2 respectively, with constant stirring in 100 °C, until a clear homogenous liquid was formed. With each chemical, two different aqueous solution concentrations, 30-w% and 15-w%, were prepared. With Merck pH-indicator strips, the pH-values of the 30% solutions were measured to be 12 (SS) , 8.5 (DAP) and 9 (DES).

Oven-dry veneers were either vacuum impregnated or soaked in the chemicals for 3 or 24 hours to get an overview on how the chemical uptake was affected by the treatment type. The vacuum impregnation was carried out in a vacuum of 50 mbar absolute pressure for one hour, which was determined to be sufficient for a high chemical uptake of the 0.8 mm veneers, but without causing problems with the changing viscosity of the sodium silicate or evaporation of DAP solution. All treatments were carried out in room temperature. In total this resulted in six different treatments, as demonstrated in Figure 6. Preliminary tests that involved brushing the chemicals onto the veneer surface resulted in a negligible chemical uptake and were thus discarded for the actual tests. Due to the large number of

different treatments and samples, some of the tests performed only on the impregnation treated veneers.

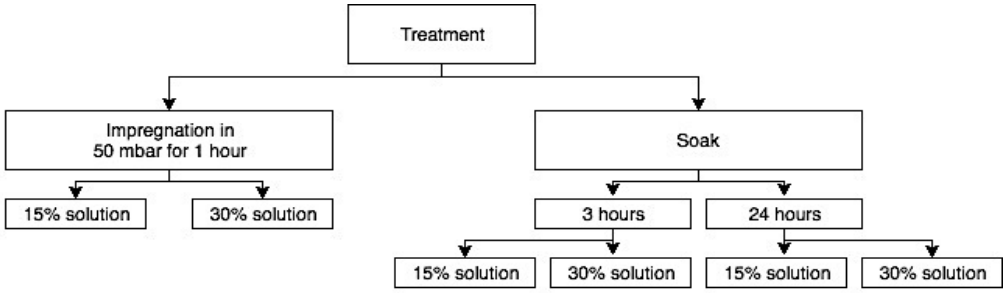



**Figure 6.** Schematic illustration of all the different treatment types.

After each treatment the veneers were gently patted dry with a paper tower and dried in 103 °C for 24 hours between metallic grates, which allowed air flow around the samples. WPG values were determined for each veneer according to Equation 1, where $M_m$ is the oven dry mass of modified wood and $M_u$ the oven dry mass of unmodified wood.

$$\text{WPG}\ (\%) = \frac{M_m - M_u}{M_u} \times 100 \qquad (\mathbf{1})$$

After this the veneers were cut to dimensions of 20 x 117 $mm^2$ and conditioned in RH 35% and 20 °C, until the equilibrium moisture content (EMC) of the reference veneers was on average 5.9%, which is suitable for the ABES testing.

## 5.3 SEM-EDX compound analysis

To evaluate the distribution of chemicals within the veneers, SEM imaging combined with compound analysis was carried out for 30% solution impregnated samples with Hitachi S-4800 field-emission-scanning electron microscope (FE-SEM) equipped with an Apollo variable pressure SEM equipped with energy dispersive X-ray detector (EDX). Oven-dry veneers were prepared for imaging by slicing the transverse surface with a scalpel and attaching them on an aluminum sample tray with the cut side pointing upwards. The samples were then coated with Gatan Precision Etching Coating System (model 682, Sweden) for 15 minutes and 20 rounds per minute spinning rate using silver-platinum mixture as the conductor. The resolution of the

SEM-EDX images was 251×270 pixels, maximum dead time 20 seconds and the maximum acceleration voltage 20 kV. The produced backscattered electron and EDX mapping images were compared to analyze the distribution of the chemicals.

## 5.4 Leaching tests

Leaching of the chemicals was assessed by applying the method EN 84:1997 "Wood preservatives. Accelerated ageing of treated wood prior to biological testing. Leaching procedure". Oven-dry samples were first vacuum impregnated with 400 ml of deionized water in 40 mbar vacuum for 20 minutes. After the releasing the vacuum the samples were left in the vessels for two hours. The water was then replaced with 400 ml of fresh deionized water and the sample immersion was continued for 14 days in room temperature. During this the water was changed nine times in total: at the end of the first and second day of immersion and later at intervals of one to three days. The samples were then dried in 103 °C for 24 hours and mass losses were determined from ten replicates for each treatment. Amount of leachant from wood after testing was determined according to Equation 2, where $M_{bl}$ is the oven-dry mass of sample before leaching and $M_{al}$ the oven-dry mass of sample after leaching (Sloot *et al.*, 1997; Baysal *et al.*, 2005; Altun *et al.*, 2010).

$$\text{Leachant } (\%) = \frac{M_{bl} - M_{al}}{M_{bl}} \times 100 \qquad (\mathbf{2})$$

## 5.5 Thermogravimetric analysis

Thermogravimetric analysis was performed using Thermo Gravimetric Analyzer Q500 TGA (TA Instruments) device. Before analysis the oven-dry samples were first ground to a fine powder in a Wiley mill (1 mm mesh) and for each test 10-15 mg were placed in the sample furnace chamber of the instrument. The analysis was carried out under nitrogen gas at purge rate of 60 ml/min and heating rate of 10 °C per minute, ranging from room temperature to 600 °C. The mass loss was recorded as a function of temperature, as well as the onset point, temperature at the maximum rate of decomposition and the final amount of residue. Due to the large number of samples, only one measurement was performed for each treatment type. Results were analyzed and graphs drawn using the QSeries Universal Analysis 2000 software.

## 5.6 Fire resistance

Fire resistance was studied based on the procedure described by Pries and Mai (2013). Prior to testing the samples were conditioned in RH 35% and 20 °C. During testing the samples were clamped into a holder, which was placed on top of a balance as presented in Figure 7. They were positioned so that they were at an angle of 45° to the vertical and their tip was ignited and kept in contact with a lighter for 20 seconds. The flame height, strength and distance from the sample were kept constant throughout the testing and three replicates were used per treatment. Combustion of the samples was videotaped and the weight was recorded at 5 second intervals and graphed as a function of time, until the mass remained constant. The combustion time and type, whether the sample was flaming or glowing, were also recorded.

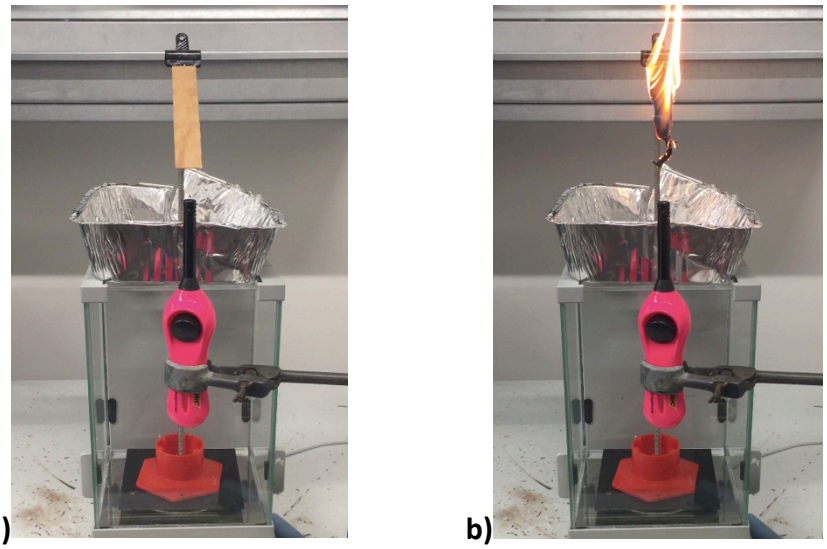



**Figure 7.** Fire resistance test system **a)** before test **b)** during measurement after the ignition source was turned off.

## 5.7 Contact angle measurements

To assess the wettability of the samples, contact angle measurements were performed with Cam 200 Optical Contact Angle Meter (serial number 7238, KSV Instruments Ltd) device, using distilled water as probe fluid. The samples were set on an adjustable table and a droplet of water was dispensed to the sample surface. A camera recorded the adsorption of the droplet with an adjustable frequency, across

the grain line. The contact angle measures were carried out in normal room air temperature and uncontrolled humidity. The volume of the water droplet was 6.7 µl and it was filmed for three minutes or until the droplet was completely adsorbed by the surface. For the first five seconds, the frame interval was 200 ms and after that 10 s until the end recording. Prior to testing, the samples were conditioned in 20 °C and (35±5)% RH to match the equilibrium moisture content used in the ABES testing. Only the vacuum impregnated treatments were selected for testing and 16 measurements were taken and analyzed for each treatment.

## 5.8 ABES bond line testing

Only vacuum impregnated samples were selected for testing. 8.6 µl drop of phenol-formaldehyde (14J025, Prefere Resins Oy, Finland) resin was dispensed to the end of one veneer sample with an electronic micropipette (HandyStep electronic, Brand GmbH + CO, Germany) and using another sample spread evenly to an area of 20 x 5 $mm^2$, which corresponds to a load of 100 $g/m^2$. As soon as the spreading was finished, the samples were placed to the ABES (Adhesive Evaluation Systems, Incorporated) test device which is presented in Figure 8.

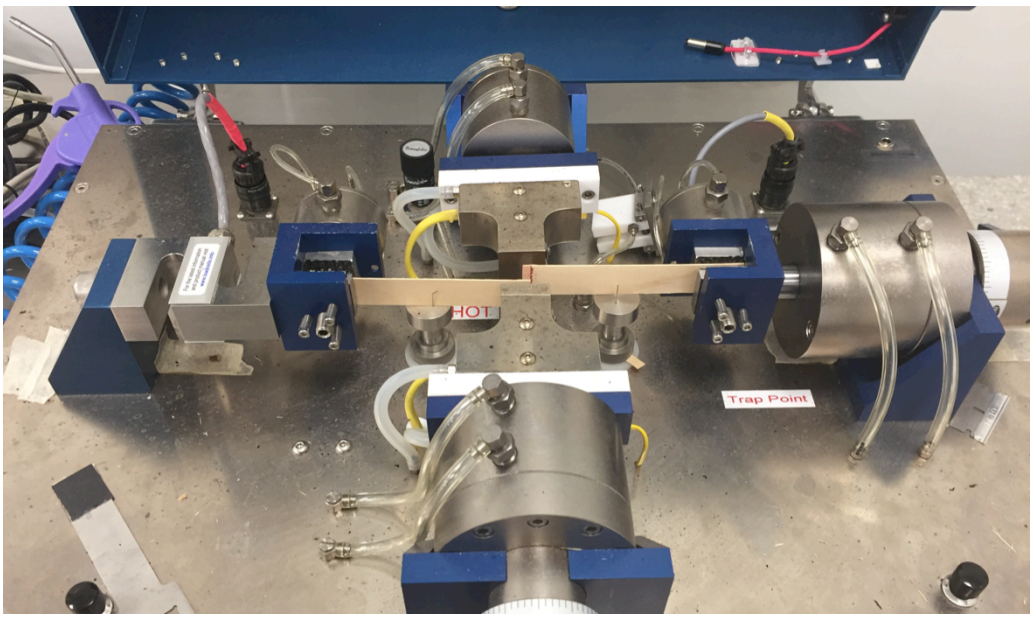



**Figure 8.** ABES device used for testing the adhesion of veneers. Glue is spread on surface area of 5 x 20 $mm^2$ and pressed together. After pressing the heads on left and right pull from the sample ends and measure shear strength of the glue bond line.

The time between the glue spread and the start of the pressing was constant, which was approximately 15 seconds. The hot plate temperature was 130 °C, press compression 2 MPa and four different press times were used: 60, 100, 140 and 180 seconds. Shear strength in the grain direction was measured immediately after the pressing. Seven replicates were used for each analyzed treatment.

# 6 RESULTS AND DISCUSSION

## 6.1 Chemical uptake and physical changes in veneers

WPG values of the veneers are presented in Figure 9. As could be expected, in all cases the WPG increased along with the concentration. During the soak treatments higher WPG values correlated with soaking treatment times. In general, vacuum impregnation was more effective than soaking in introducing the chemical into the veneers. This is acknowledged by Mali (1979, p. 71), who argued that in soaking treatments the chemical uptake is typically too slight to have much effect on the wood properties. An exception was the 30% solution 24 hour soaked DES samples, which had the highest WPG value of all samples. Overall DES had the highest WPG values, although with impregnation treatments there was little difference between DES and DAP. Di Blasi *et al.* (2007) reported much higher WPG values for wood samples soaked in DAP solution: WPG of wood blocks soaked for 3 hours in 15% DAP solution was 20%, which is over 17% higher than in this work. There were slight differences in the treatment protocol (e.g. sample washing with hot water before treatment, constant stirring during immersion) but this was unexpected. Additionally, in this work the treatments were done on oven-dry veneers. High moisture content has a positive effect on the diffusive impregnation process of fire retardant chemicals (Bekhta *et al*., 2016) and therefore the use of dry veneers was likely to reduce the chemical uptake.

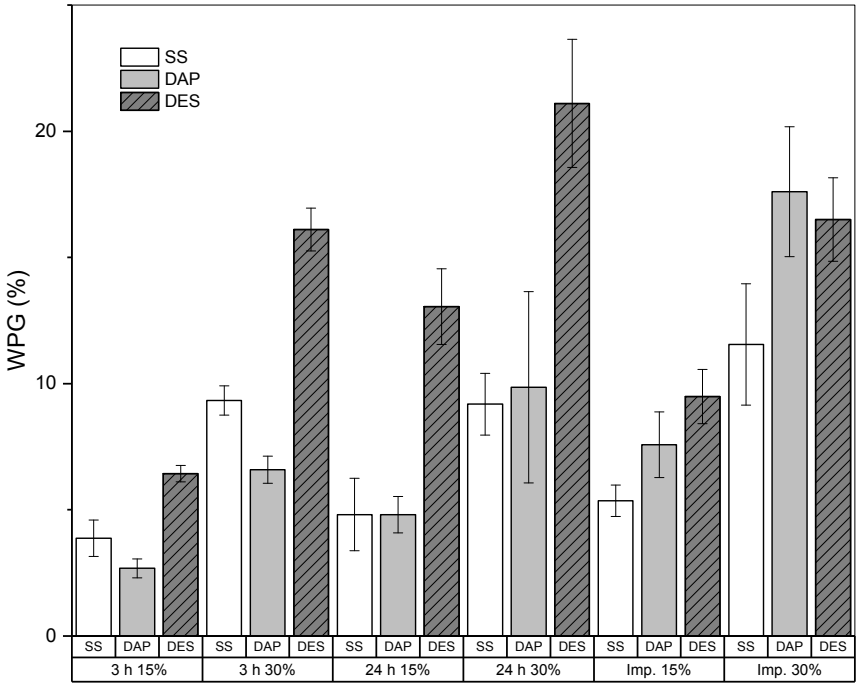



**Figure 9.** WPG values after treatment and 24 hour drying in 103 °C.

In this work, the treatment methods and conditions were compromised to make it possible to carry out the experiments with all three different chemicals. In literature, chemical uptake is often reported as the wet retention, which was not measured in this work due to viscosity changes of SS solutions and DAP solution evaporation and salt crystallization in the 24 hour soak treatments. Additionally, the chemicals are rarely used alone, but rather in combination with other chemicals to achieve the best possible fire protection or better fixation. The results showed a high amount of variation, especially in the impregnation treatments and 24 hour soak treatments. Because of the low mass of the sample veneers, even slight errors in measurement may have resulted in a relatively high chemical uptake.

EMC of the veneers was calculated based on the oven-dry mass and the mass after the equilibrium was reached at 20 °C and 35% RH. EMC of the SS modified samples was the highest with over 7% EMC in RH 35% and 20 °C, which was clearly higher than that of reference (5.9%). DES and DAP had a smaller effect on the EMC, resulting in 5.2% (DES) and 6.6% (DAP) EMC. According to Mali (1979, p.78) SS and DAP are highly hygroscopic, so changes in EMC were to be expected in comparison with the reference. The modifications also resulted in visible color changes in all samples, as is demonstrated in Figure 10, where the reference veneer is on the background. The

effect was most dramatic with DAP modification, which caused notable darkening in all samples and especially with the 15% impregnated sample. SS modification resulted in slightly yellow tone in the veneers, while DES turned the veneers slightly darker. Fire retardant treatments are known to cause darkening or discoloration in wood (Forest Service & Products Laboratory, 2010, p.16), but the mechanism remains unknown.

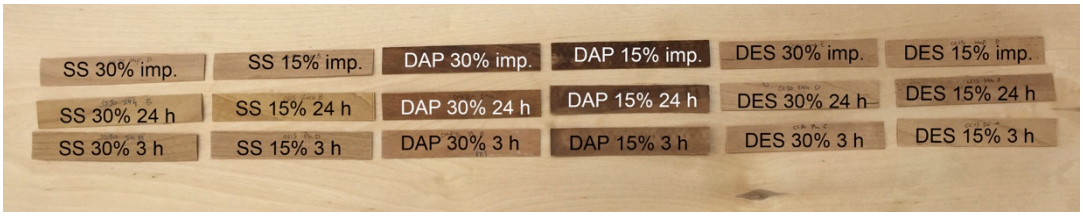



**Figure 10.** Discoloration of the modified veneers. Reference birch veneer is on the background.

## 6.2 SEM-EDX compound analysis

SEM-EDX analysis was performed on all 30% impregnated samples, but due to coating failure no image of the SS samples could be produced. However, there were clear differences between the DAP and DES modified samples. The distribution of DAP in the veneer samples was detected from the Kα elemental peaks of phosphorous and marked in Figure 11 in color red. The chemical was mostly concentrated to the veneer surface, but some of the vessels present in the birch also showed a high concentration of chemical. Wang *et al.* (2016) reported similar accumulation of fire retardant containing nitrogen and phosphorous to the vessels of the wood material by SEM-EDX analysis.

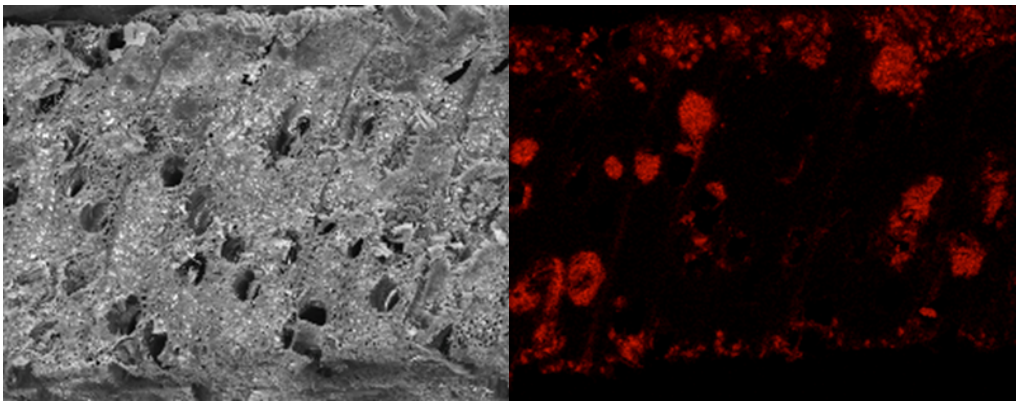


**Figure 11.** Electron backscattered image (left) and SEM-EDX compound map of phosphorous (right) of from 30% DAP impregnated sample..

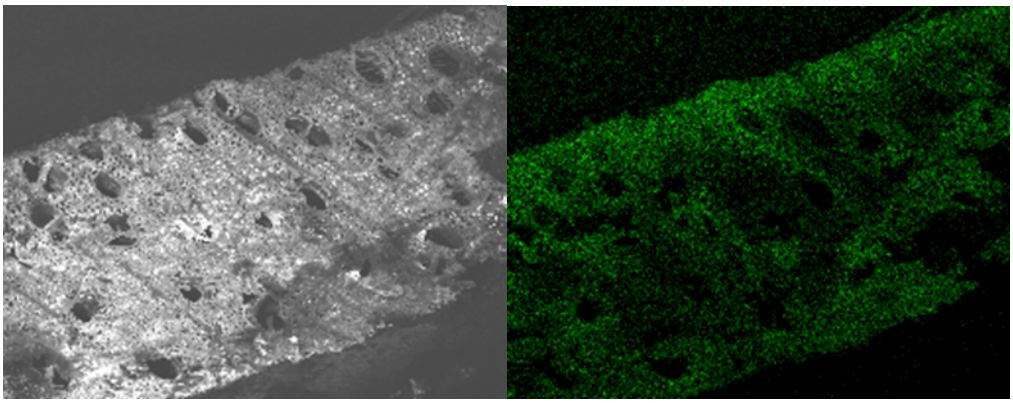


**Figure 12.** Electron backscattered image (left) and SEM-EDX compound map of chloride (right) from 30% DES impregnated sample.

For DES modified samples, Kα elemental peaks of chloride were recorded and marked in green in Figure 12. DES resulted in nearly full chemical penetration throughout the cross-sectional area of the veneer, which explains the high WPG values observed. The surfaces showed slightly higher concentration of chemical, but chloride particles and therefore DES were present in all parts of the sample. Unlike with the DAP modified sample, the vessels mainly remained free of chemical.

In general, improvement of fire resistance can be achieved by filling the lumens in wood with chemical compounds. However, to achieve permanent results the chemical compounds need to incorporated into the cell wall, which can be detected from swelling of the wood material due to reaction or infrared spectroscopy analysis. Material that is accumulated only to the veneer surface can be considered as a coating, which may leach from the wood surface if it is water soluble. (Rowell, 1983; Mai & Militz, 2004; Hill, 2006, p. 43) Due to the low resolution of the SEM-EDX images, specific data about the fire retardant distribution on a cellular level could not be obtained. In future research, this should be determined for SS, DAP and DES modified material. Knowledge about whether the chemical is present in the lumens or cell wall would be important for a better understanding of the fire retardant chemical and wood interactions.

## 6.3 Results from leaching tests

Results from leaching tests are presented in Figure 13. Amount of leachant from every SS, DAP and DES modified sample was calculated according to Equation 2 and

compared with the WPG values. Amount of leachant from reference was 2.5%, which was likely due to the removal of extractives and loose material (e.g. dust). It was found that in more than half of the samples, the fire retardant chemicals were leached out completely. Only seven samples showed some resistance against leaching, which are those under the plotted y=x line, marking the balance between the leachant and WPG values. The samples with the highest chemical load after leaching were 30% SS and DES impregnated samples, which had 4.1% and 3.2% of chemical left after leaching. SS 30% 3 hours soaked samples resulted in 2.6% of remaining chemical, DAP 30% 24 hours soaked in 1.9%, DES 30% 3 h in 1.3% and all the rest in less than 1% or no chemical present in the wood material after leaching. However, even the highest amount of remaining chemical of the SS and DES 30% impregnated samples is likely too low to provide any protection against fire, as is discussed in Chapters 6.4 and 6.5.

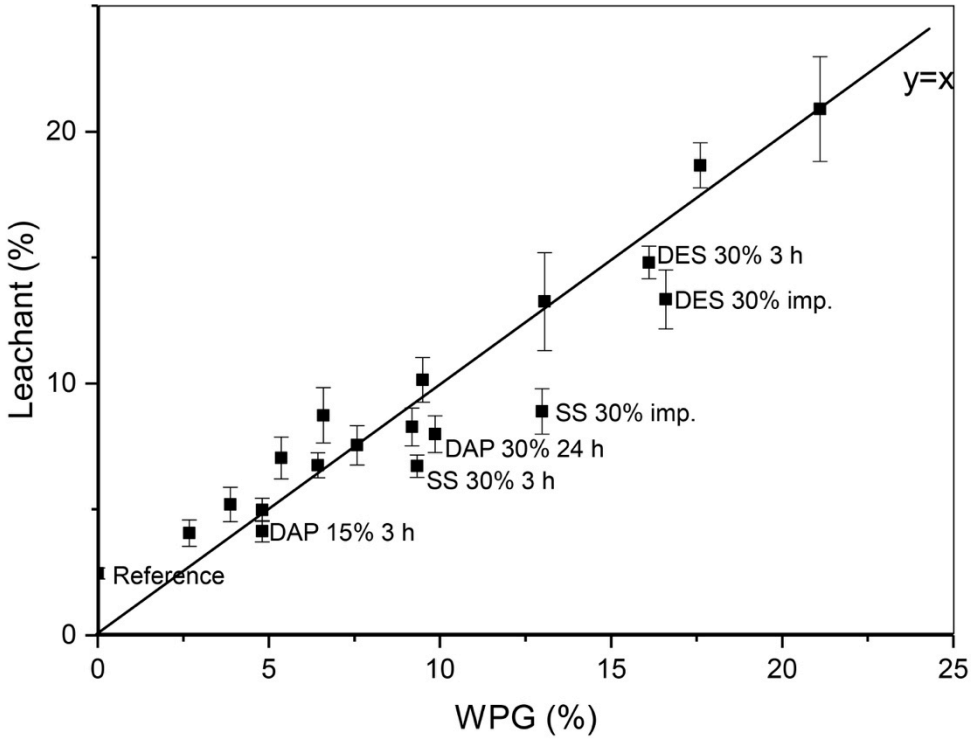



**Figure 13.** Results from EN 84 leaching test, where the average amount of leachant from every sample is plotted against the WPG values.

The results are similar as those of Furuno *et al.* (1992), who found that a considerable amount of SS was washed out of impregnated wood samples by the end of leaching tests. This is due to the chemical nature of SS: it is highly soluble in water, because it

is strongly alkaline and readily forms anionic silanolate groups, where the silicon particle is connected with a hydroxyl group (Pries & Mai, 2013). As all inorganic salts, DAP is also susceptible to leaching, so poor performance was to be expected (Holmes, 1977; Östman *et al*., 2001; Östman & Tsantaridis, 2016). Sample dimensions have a major influence on the leaching process. Samples with large surface area to volume-ratio, such as thin veneers, allow proportionately more wood for leaching and the distance that chemical components have to diffuse to the wood surface is decreased (Cooper, 1994). Therefore, the results from this work do not necessarily assimilate with the leaching behavior of real-size plywood panels.

As was concluded in the literary review, EN 84 is one of the most severe leaching test protocols. More information about the leaching behavior of samples could have been obtained, if the leaching waters had been chemically analyzed. Instead of simply noting the complete leaching of low WPG samples, specific leaching rates could have been assessed. The change in leaching rate could be noticed visually: during the first few water changes, there were notable differences in the immersion water color. SS and DES turned the water strongly yellow, while DAP caused the water to turn light gray. The color changes gradually decreased as the water was changed and by the fourth water change the color remained clear in all cases. Additionally, the color of the wood samples remained unaffected by the leaching.

As was concluded in the literary review, leaching of SS is often reduced with the use of some fixing agent, typically an organic or boric acid. Gelation of sodium silicate and formation of polymeric species is known to occur in the presence of acids and acid-forming compounds and the crosslinking and packing of these polymers is even increased in dry conditions (Merrill & Spencer, 1949; Brinker & Scherer, 1985). Above 140 °C, thermal degradation of hemicelluloses results in the production of acetic and formic acids, forming a low-pH environment in the wood material (Hill, 2006, p. 103; Sundqvist *et al*., 2006). Therefore the potential of thermal modification of wood in polymerizing sodium silicate into the wood structure could be explored as a potential fixation process. It may be speculated that the addition of sodium silicate to the thermal modification process could provide increased fire resistance to thermally modified wood products. Further work could be done on the subject.

## 6.4 Results from thermogravimetric analysis

Thermal analysis revealed that all treatments had an effect on the veneer pyrolysis behavior. Results from TGA testing of impregnated samples, pure chemicals and reference are summarized in Table 1.

**Table 1.** Summary of TGA results of reference, impregnated samples and pure chemicals used, where $T_{onset}$ is the onset temperature, $T_{max}$ the temperature at which the rate of pyrolysis is at maximum and RM the relative amount of final residue.

| **Treatment** | **$T_{onset}$ (°C)** | **$T_{max}$ (°C)** | **RM (%)** |
|---|---|---|---|
| **Reference** | **257** | **362** | **13.1** |
| SS pure (aq) | 116 | 129 | 36.4 |
| SS 30% imp. | 257 | 305 | 33.5 |
| SS 15% imp. | 262 | 308 | 27.3 |
| DAP pure | 146 | 600 | 31.3 |
| DAP 30% imp. | 237.53 | 278.26 | 30.45 |
| DAP 15% imp. | 201 | 274 | 30.4 |
| Choline chloride pure | 307 | 327 | 0.3 |
| Urea pure | 167 | 205 | 0 |
| DES 30% imp. | 159 | 359 | 12.7 |
| DES 15% imp. | 159 | 364 | 12.3 |

In this work, the reference birch sample behaved similarly as in the works of Grønli *et al*. (2002) and Tapasvi *et al.* (2013). Differential thermogravimetry (DTG) curve of the TGA data presents the differential mass loss over time and is a tool for analyzing the various stages of decomposition. The DTG curve of reference birch sample, presented together with 30% SS impregnated sample in Figure 14, showed a distinct shoulder at 275-325 °C. This corresponded mainly to degradation of hemicellulose, but also to the beginning of overlapping cellulose decomposition. The main peak of DTG curve at 362 °C is the maximum rate of decomposition, $T_{max}$, and is associated mainly with cellulose decomposition, which continued until 270 °C. This was followed by a long tail of slow mass loss, which corresponded to the wide temperature range of lignin decomposition.

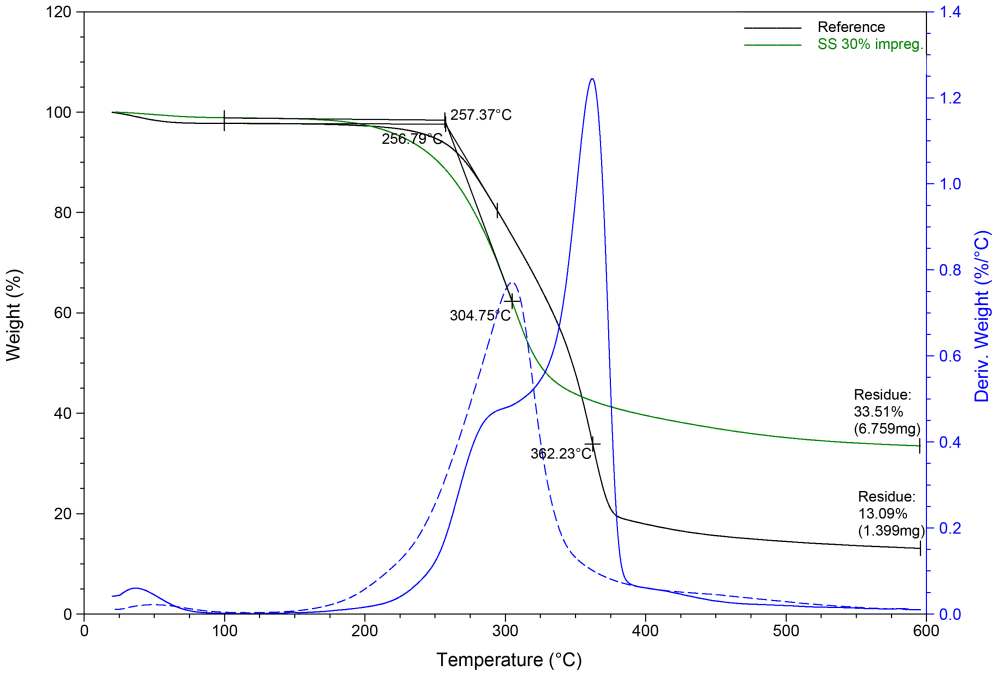



**Figure 14.** TGA and DTG curves of reference and 30% SS impregnated sample.

The effectiveness of fire retardant chemicals can be evaluated from TGA data through a decrease in the value of the onset point, $T_{onset}$, and an increase in the amount of produced charcoal, which is indirectly indicates a reduction in the amount of combustible gases (Rowell, 2013, p.141). TGA analysis revealed that the presence of SS had barely any effect on the onset temperature. Onset of the SS 30% impregnated veneer (257 °C) was practically equal to that of reference. Overall the onset temperature of SS samples did not vary more than 10 °C, regardless of the WPG of the sample veneers. WPG value also had little effect on the temperature of maximum rate of decomposition, $T_{max}$, which was within 293-308 °C for all SS treated samples. However, this is approximately 60 °C lower than the $T_{max}$ of the reference sample. SS treatment shifted the pyrolysis pathway to the direction of lower temperatures, which was also noted by Qu *et al.* (2011), who found similar $T_{max}$ values with 20% SS soak treated veneers. SS impregnation also increased the amount of final residue from 13.1% of reference to 33.5% of 30% impregnated samples and 27.3% of 15% impregnated samples. To evaluate the impact of fire retardant chemicals on the char yield, the residual mass (RM) of the samples was compared with the RM of pure chemicals and reference. The calculated theoretical RM values of SS impregnated samples did not compare with the actual measured value. The RM of 30% and 15% SS impregnated samples was not equivalent to the sum of the wood char and

incorporated SS. This might indicate that in addition to a weight increase by residual SS, an increased char formation occurred for SS impregnated samples. However, in a recent study Xiao *et al.* (2016) found alkaline silicate dispersions to have no effect on the char yield, so further study on the subject is needed.

In this work, pure SS was used in the veneer modifications in an aqueous form and the residue of the pure chemical after TGA testing is presented in Figure 15. White, hard and foam-like residue was formed, which expanded in volume during testing. This foaming of SS at elevated temperatures is a well known phenomena and Subasri & Näfe (2007) reported that in this takes place at 400-750 °C, after which the porous structure collapses. They also found that pure SS remains amorphous up to 300 °C, which is in the range of the measured $T_{max}$ values of all SS modified samples (293-308 °C) in this work. The residue from 30% SS impregnated veneer sample showed different structure than the DAP and DES modified samples. Unlike DAP and DES sample residue, the milled veneer remains of SS sample did not collapse to powder-like form. SS seemed to maintain the structure intact and form a protective layer on the wood material surface, as it is stated to function in the literature (Kozlowski & Wladyka-Przybylak, 2000; Lowden & Hull, 2013).

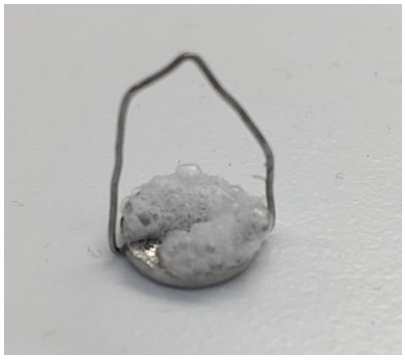
**a)**  **b)** 

**Figure 15.** Residue from the testing of **a)** pure SS and **b)** from the testing of SS 30% impregnated sample.

TGA and DTG curves of 30% solution impregnated DAP samples are presented in Figure 16. Modification with DAP lowered the $T_{onset}$ by an average of 28 °C, which was more than in the case of SS. WPG of the sample veneers had an effect on the $T_{onset}$, which was lowered more in the 15% impregnation and 24 hour soak treatments than in the 30% treatment. This was unexpected, as stronger treatments and higher WPG values were assumed to be more effective and therefore lower the $T_{onset}$ more

compared to the reference. However, this behavior was later evened out in the $T_{max}$ values, which were quite similar independent of the differences in WPG values and in the range of 273-286 °C for each concentration and treatment. DAP also increased the amount of RM by 17% compared to the reference. The effect of DAP on the char yield was analyzed similarly as with SS, but no significant differences were noticed. However, Di Blasi *et al.* (2007) reported that DAP treatment increased the char yield of modified fir wood samples. Additionally, the RM of 30% and 15% impregnated samples was 30% for both, which based on the different WPG values was unexpected. If the RM consisted mainly of the DAP salt itself, which at 600 °C is still at the stage of rapid decomposition, the RM should depend on the WPG of the samples. Overall the pyrolysis analysis results of DAP results are in line with the work of Shafidazeh *et al.* (1984), who found DAP in a comparative study of 21 fire retardant chemicals to be one of the most effective in increasing the amount of RM and reducing the amount of volatile gases. Unlike with SS modified samples, individual wood chip shapes could not be identified from the DAP sample residue, which is resented in Figure 17. The residue was more powder-like and the structure of the milled samples had collapsed completely.

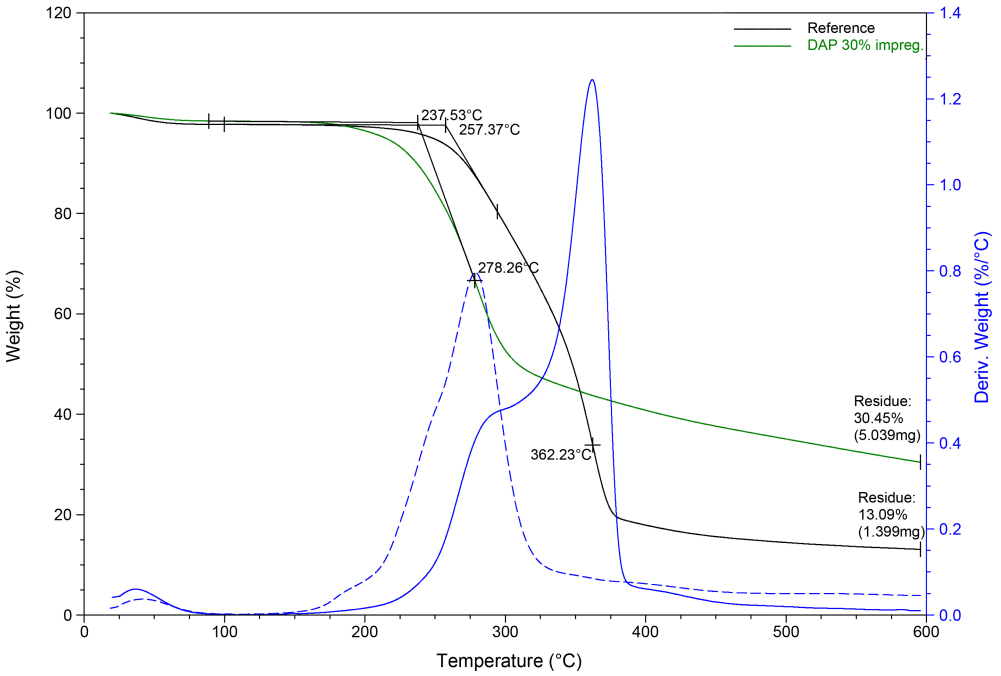



**Figure 16.** TGA and DTG curves of reference and 30% DAP solution impregnated sample.

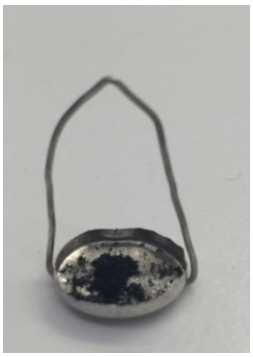


**Figure 17.**. Residue from the 30% DAP impregnated sample.

The pyrolysis of samples impregnated with a 30% solution of DES proceeded differently compared to SS and DAP treated samples, as presented in Figure 18. Three peaks appeared in the decomposition DTG curve: at 185 °C, 250 °C and the last one at 359 °C, which was the $T_{max}$ of 30% DES impregnated sample. The first and second peaks corresponded to the two rapid stages in urea decomposition (Schaber *et al.*, 2004). DES modification also had the most dramatic effect on the $T_{onset}$, which was lowered by an average of 96 °C, in spite of that the measured $T_{onset}$ of pure choline chloride and urea components (307 °C and 167 °C) were higher than those of SS (116 °C and 146 °C). WPG of the veneers had little effect on the $T_{onset}$ values, as they were all in the narrow range of 159-165 °C. The same applied for the $T_{max}$ of DES modified samples, which were all within 345-362 °C range. This is almost identical to the $T_{max}$ of reference, as can be seen from the overlapping DTG curve. The difference between $T_{onset}$ and $T_{max}$ of DES modified samples was over 190 °C, which was several times more than of SS (46 °C) and DAP (50 °C). DES modification appeared to modify the pyrolysis pathway more dramatically than SS or DAP, but the differences with DES and reference diminished after approximately 325 °C, which marks the end of hemicelluloses degradation range. RM of DES (12.7%) was essentially the same as that of reference, because the pure choline chloride and urea components were completely degraded before 400 °C.

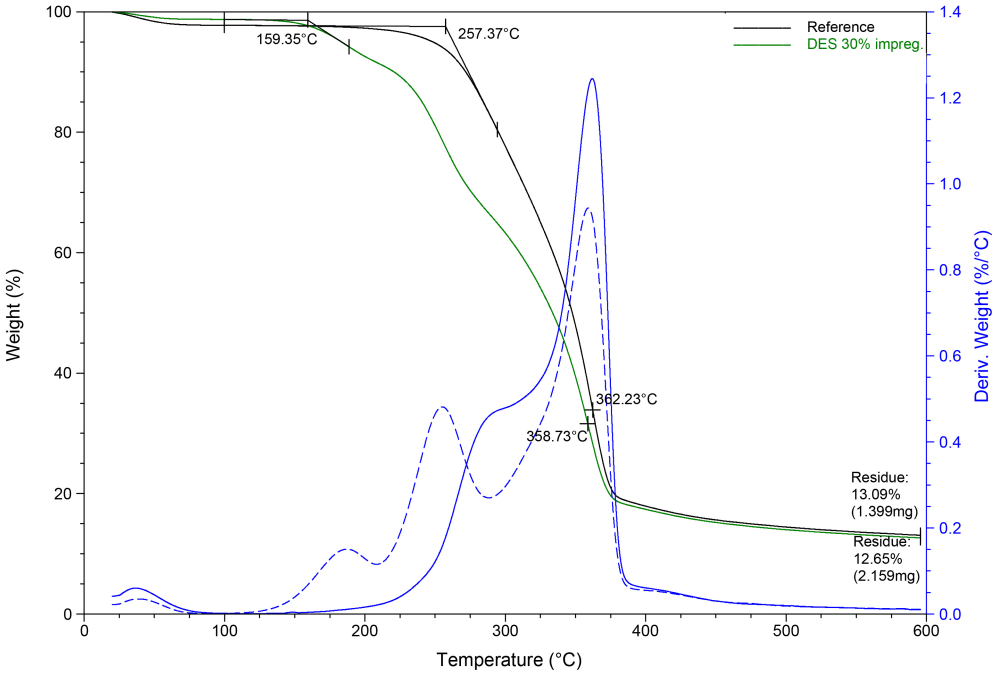



**Figure 18.** TGA and DTG curves of reference and 30% DES impregnated sample.

## 6.5 Results from fire resistance testing

The fire resistance test revealed a reduction in mass loss for all of the modified samples, as presented in Figure 19 and Figure 20. Reference samples decomposed completely, resulting in only 2% of RM, which was deposited in the sample holder. DES modified samples had a similar mass loss pattern with 15% and 30% solution impregnated veneers, both resulting in 13-15% of RM. Interestingly, 15% impregnated DES samples decomposed upon touch in the sample collecting after testing, but the 30% impregnated samples did not, even though the RM was equal for both. The slight improvement in fire resistance by DES was in line with the TGA results, where a reduction in $T_{onset}$ occurred, but $T_{max}$ values were of the level of the reference. The mechanism behind the fire resistance of DES remains unknown, but could be investigated further in future work. Urea is known to release large amounts of incombustible gases below the temperature, where the main wood pyrolysis reactions start, which could explain the notable reduction of $T_{onset}$ in TGA, but only a slight effect in the real combustion behavior of DES modified samples (Pizzi *et al.*, 2016, p. 40).

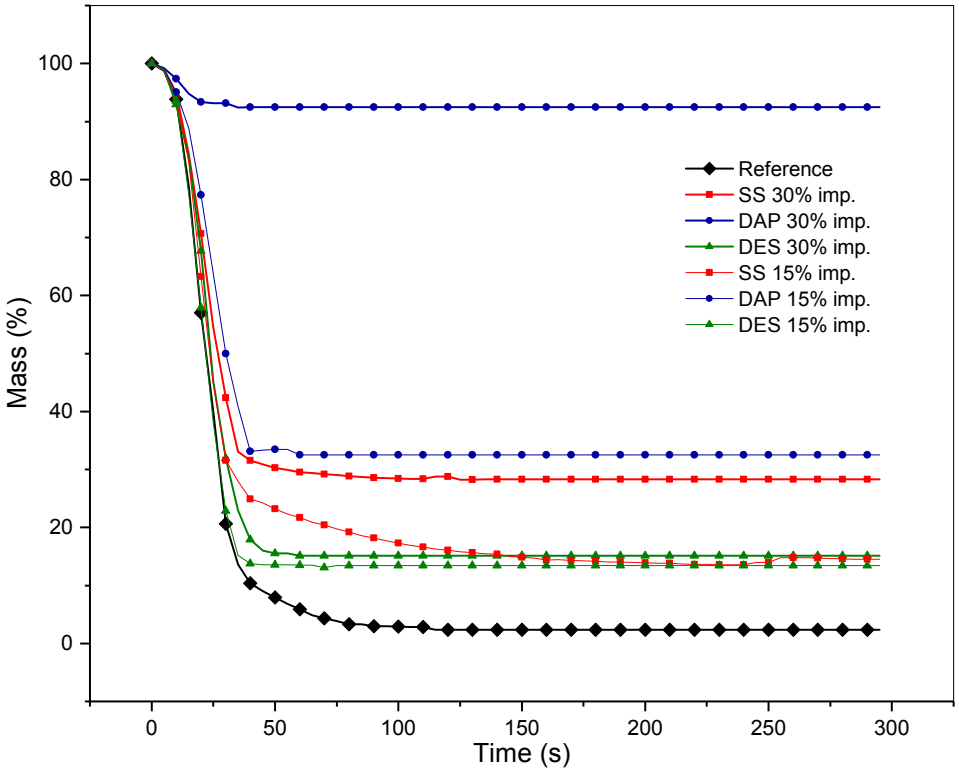
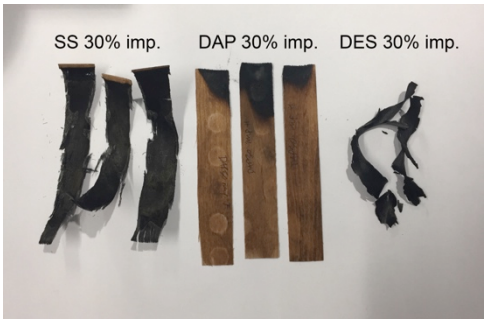



**Figure 19.** Mass loss curves of 30w-% and 15w-% impregnated samples in fire resistance test.

Unlike in TGA, the effect of treatment concentration was very visible with SS and DAP treated samples. 15% solution impregnated SS samples resulted in 14% of RM, but the 30% solution impregnated veneers improved the material protection so that the amount of RM was 28%, resulting in an increase of 13%. 15% SS impregnation resulted in the same amount of RM as the DES modification, but the rate of mass loss was notably lower. With DAP the effect of chemical uptake was the most prominent, as the 30% solution treatment inhibited the ignition almost completely. Mass loss of less than 1% occurred after the source of ignition was removed and the amount of RM was 92%, which is significantly higher than with any of the other treatments. The wood was strongly charred close to the source of ignition, but the flames did not spread across the sample. Rate of mass loss, which is the slope at the area of rapid combustion, was also smaller with DAP modified samples than with the other treatments. 15% DAP solution impregnation was the second most effective treatment, resulting in 33% of RM, and was the only 15% solution impregnated sample that did not decompose completely after testing. The results are in line with information obtained from the TGA analysis, where DAP caused a reduction in the $T_{onset}$ and shifted the $T_{max}$ the most to the lower temperatures. This is an indicator of

increased char formation, which was clearly visible in the actual fire resistance testing.

**a)** 


**b)** 

**Figure 20.** Residue from fire resistance testing of **a)** 30% solution impregnated samples **b)** only 15% DAP impregnated samples. All of the other samples decomposed completely when removed from the sample holder, so no residue could be collected.

Durations of flaming and glowing combustions of impregnated samples are presented in Figure 21. Little variation occurred in the measured duration of flaming combustion between different samples, except for 30% DAP solution impregnated veneers. They proved to be practically non-flammable and the flaming ceased immediately, when the source of ignition was removed after 20 seconds. DAP modification also completely prevented glowing combustion. The results correlate with the work of Hunt & Garratt, who according to Mali (1979, p. 64) found DAP to be the most effective chemical in reducing flaming and glowing combustion in a comparative study of 130 chemicals. DES modification also reduced the glow-time by over a half. However, SS treatment did not reduce the glowing but in fact prolonged it, especially with the 15% solution impregnation. More variation occurred in the glowing combustion durations than with flaming combustion.

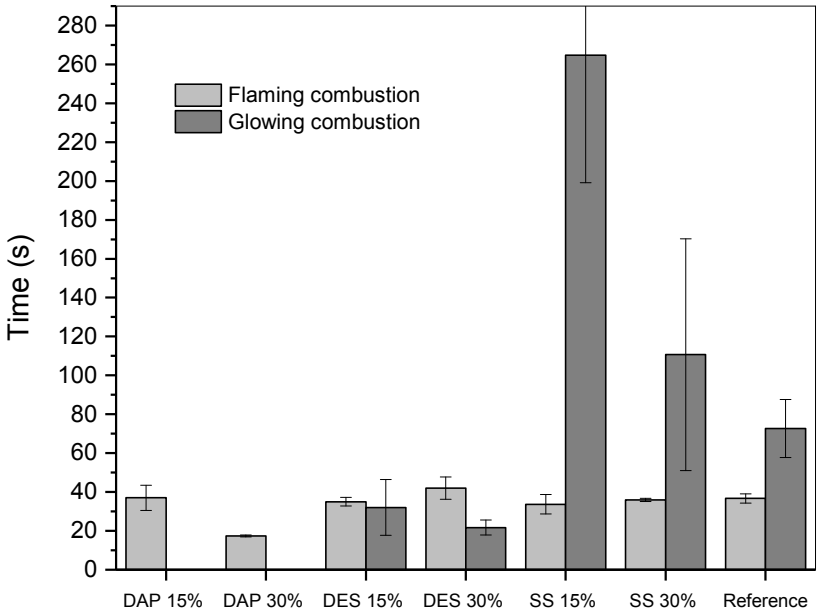



**Figure 21.** Durations of flaming and glowing combustion of fire retardant treated samples.

The evaluation of flaming combustion could have been more accurate, had there been a Bunsen burner and not a regular yellow flame lighter. It should be noted that the data variation is relatively high, due to a limited number of repetitive measurements and the uncontrolled test environment leading to variations in airflow.

Based on the TGA and fire resistance results, a combination of SS and DES treatments could be worth investigating as a fire retardant chemical. Although the synergism between the two is unknown, DES could potentially balance the highly increased glowing combustion of SS modified wood and lower the $T_{onset}$ and affect the pyrolysis pathway. SS could in turn lower the $T_{max}$ of DES and increase the fire resistance of the whole system.

## 6.6 Effect of fire retardant chemicals on veneer wettability

Results from contact angle testing of 15% and 30% solution impregnated SS, DAP and DES samples are presented in Figure 22. The reference sample behaved similarly as in the work of Rohumaa *et al.* (2014), where the initial contact angle of similarly processed veneers was also approximately 120° and steadily decreased over time. In general, all of the treatments lowered the contact angle value compared to the

reference. This was most visible with SS impregnated samples, which completely absorbed the water droplet and also presented the highest amount of variance in the results. Higher treatment concentration and therefore higher chemical content and WPG of the veneers enhanced the behavior: 30% solution impregnated SS samples absorbed the droplet in less than 20 seconds, while the droplet on the 15% solution impregnated samples remained on the veneer surface for almost 40 seconds. Based on previous studies, this could be expected, because most alkaline silicate treatments for wood are known to increase the affinity of wood to water. (Mahltig, Swaboda, & Bo, 2008; Miyafuji & Saka, 2001; Pereyra & Giudice, 2009; Weldes & Lange, 1969)

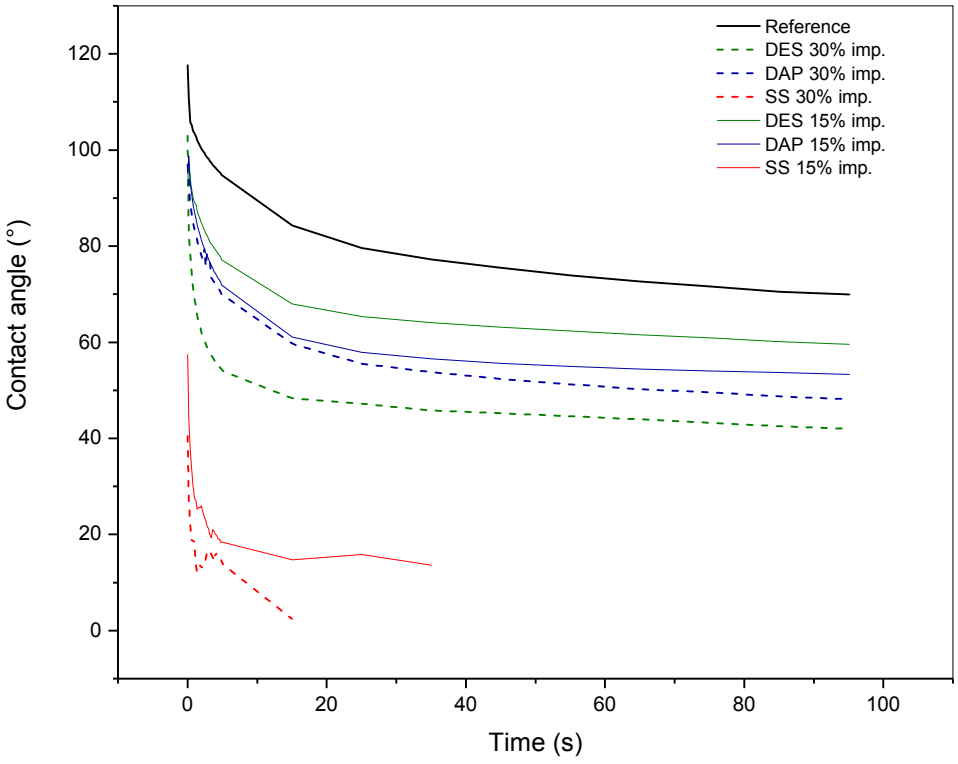



**Figure 22.** Average contact angle results of 30% and 15% solution impregnated samples.

DAP modification also decreased the contact angle of treated samples. WPG values had little effect on the sample performance, so regardless of the impregnation solution concentration all the DAP samples behaved quite similarly throughout testing. There was only a 5% difference in contact angle values of 30% and 15% solution impregnated samples after 95 seconds measurement. Because of their high solubility to water and molecular size, DAP and other inorganic salts are known to attract water and increase the moisture content of wood and therefore a decrease in

the contact angle values could be expected (LeVan & Winandy, 2007). Similar results were reported by Ayrilmis *et al*. (2009), who studied the wettability of fire retardant treated laminated veneer lumber panels dried at different temperatures. DAP impregnated panels dried at 120 °C had an initial contact angle of 84°, which is 10-12° less than what was found for the 15% and 30% DAP impregnated samples in this work. However, the small difference is likely due to the differences in drying and processing conditions.

DES modification also lowered the contact angle. The 30% and 15% solution impregnated DES samples had a 17% difference in contact angle values after 95 seconds, which is more than with DAP modified samples. Overall the sample behavior much resembled that of DAP and reference, with which the moisture absorption was stabilized after 20 seconds of measurement. The type of DES used in this work is known to be hygroscopic (Shah & Mjalli, 2014), which is likely to have caused the reduction in contact angle values.

## 6.7 Effect of fire retardant chemicals to glue bond formation in ABES testing

In Figure 23 the results from ABES testing of SS, DAP and DES samples impregnated with 30% solution are presented. The results indicate that SS and DES treatments lowered the glue bond strength compared with the reference but the differences evened out with longer press times. Curiously, the glue bond strength of reference veneer decreased after 140 seconds, which could not be explained. At 180 seconds, there is only a slight difference between the reference, SS and DES samples. Overall the SS and DES behaved similarly throughout the testing. The standard deviation of the results of the 30% solution samples overlap at any measurement points but the last one, so the results present no statistical differences. However, DAP treated samples behaved very differently. The glue bond strength increased systematically with all press times, although standard deviation was also much higher with longer press times. This is due to the fact that they also fractured from the wood, not from the glue bond, far more often than the SS or DES samples with 100-180 s press times. This indicates better adhesion, but does not provide exact information about the glue bond itself, as the numerical values are actually the strength values of the wood

material. Glue bond of the reference veneers reached the maximum value already at 100 seconds, while the DAP increased almost linearly throughout the testing. SS and DES results also increased until the last measurement point. However, there is no overlapping between the last three measurement points of reference, SS and DAP samples, so there were no significant differences.

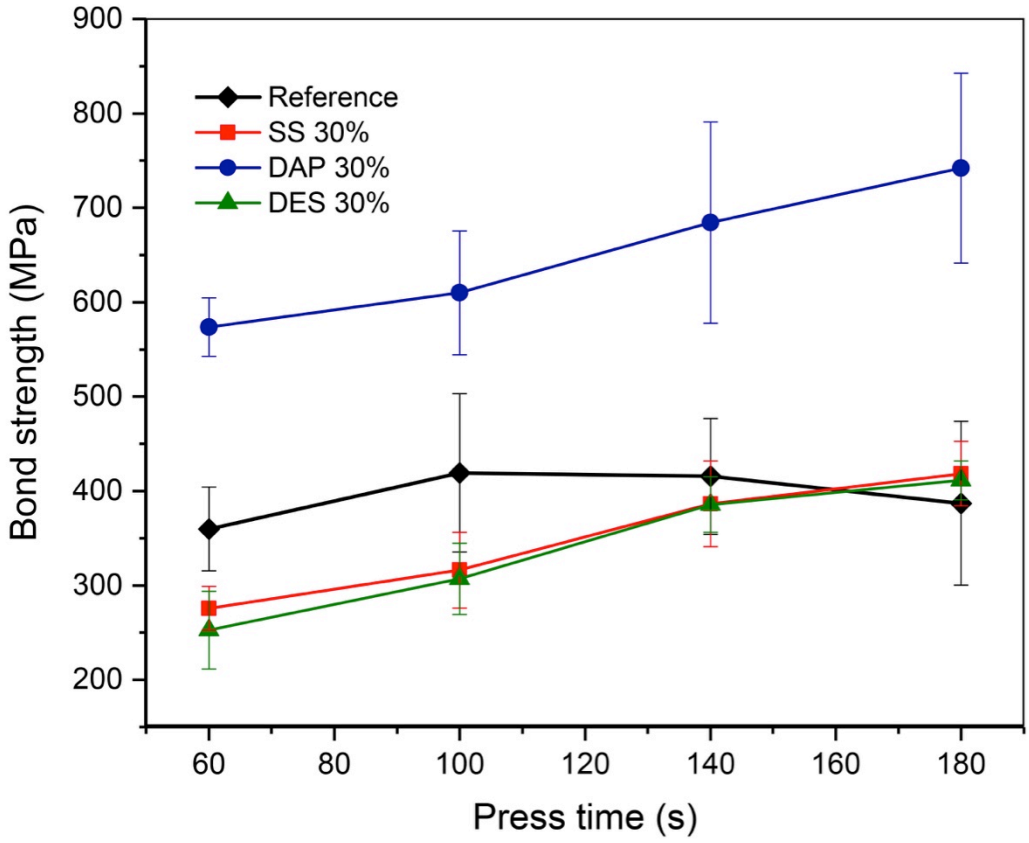



**Figure 23.** Results from ABES testing of 30% solution impregnated samples.

Results from the 15% solution impregnated SS, DAP and DES samples are presented in Figure 24. The results are similar to 30% impregnated samples, but the lower concentration affected the results to a lesser extent. Less chemical in the veneers made the behavior more alike to the reference. The DAP glue bond strength decreased compared with the 30% solution impregnation results, although the bond strength was still higher than the reference veneers. Compared with 30% solution impregnation values, the glue bond strength of SS and DES increased and even surpassed the reference with long press time. They reached the glue bond strength of reference at 140 s and surpassed that at the 180 s, although the results were still within the standard deviation. The DAP glue bond strength was again systematically

higher than the reference values at all measurement points, although there is slight overlapping with SS and reference at 100 s. Additionally, the lower concentration also caused the DAP to reach the maximum value already at 140 s and less samples broke from the wood material than with the 30-w% impregnated samples. However, the amount of cohesive failure was still high, 50% of the samples at 100-180 s press time series. This was unexpected, as Selbo (1959) found the combination of DAP and phenol formaldehyde to produce barely noticeable improvement on the glue bond compared with the reference. Compared with the 30% solution impregnated samples, the lower concentration increased the standard deviation of results in all of the treated samples.

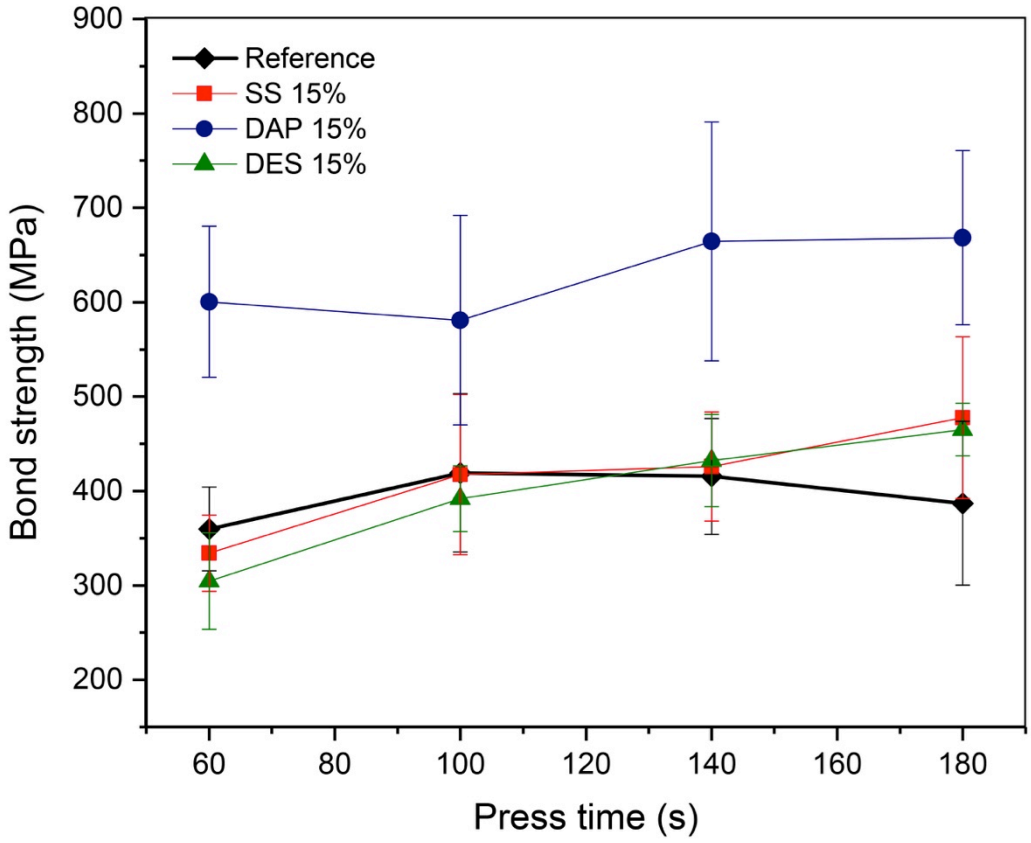



**Figure 24.** Results from ABES testing of 15% solution impregnated samples.

ABES testing had not been performed with SS, DAP or DES modified veneers before but information from mechanical plywood testing can be applied. The behavior of SS samples was as expected. It lowers the strength of the glue bond, because it forms a ceramic layer on the veneer surface and thus prevents direct glue contact with veneer. As was noticed in TGA testing, thermal degradation of SS begins at 116 °C, so

improvement of the glue bond over the longer press times may be due to gradual SS degradation, which allows for better adhesion to take place.

Based on literature, DAP was assumed to have a very small improvement on the glue bond or even weaken it. DAP releases phosphoric acid during heating, which prevents the setting of phenolic resins and weakens the wood material overall (Forest Service & Products Laboratory, 2010, p.18). In this work, DAP treatment increased the glue bond with both 30% and 15% solution impregnations. The phosphoric acid formation mentioned in literature takes place at 160-170 °C, which is higher than the 130 °C press temperature used in this work (Lowden & Hull, 2013). Therefore the slightly alkaline pH-value of DAP (8.5) may have promoted the glue bond formation, as the synthesis and curing reactions of phenol formaldehyde take place at basic conditions, and DAP had not yet decomposed into a product of lower pH (Kline *et al.*, 1946; Riedl & He, 2004).

However, neither the decomposition temperature or the pH-value explain the behavior of DES modified samples during testing. As with SS, the glue bond strength of DES modified veneers increased gradually with the press time, but according to the TGA results the decomposition of choline chloride and urea do not begin before 307 °C and 167 °C. Therefore the glue bond improvement over time cannot be explained by the gradual degradation of components. Additionally, the pH-value of DES was 9, which could have been assumed to enhance the glue bond strength, as it is in the same optimal pH-range of phenol formaldehyde glue as DAP.

Based on the wettability analysis, the nearly identical behavior of SS and DES modified samples was surprising. Compared with DES and DAP, SS clearly improved the wettability, which in the ABES testing did not translate to an enhancement in the actual glue bond strength. DES modified samples were assumed to be more alike with the DAP than SS samples, because on top of the similar pH-values they also had smaller differences in the contact angle values than SS and DES samples with each other. This demonstrates the importance of actual glue bond strength testing instead of using only wettability analysis in evaluating the adhesion performance of different materials.

# 7 CONCLUSIONS

The purpose of this thesis was to investigate and compare the effects of potential fire retardant chemicals on birch veneer properties. Three chemicals were selected for testing: SS, DAP and DES, of which DAP and SS were known to increase the fire resistance of wood, but little was known about their impact on adhesion or wettability. Veneer modification with DES was attempted for the first time. In the pre-tests several application methods were attempted and based on the results, modifications by 3 hour and 24 hour soaking and impregnation with 15% and 30% chemical solutions were selected for actual testing and WPG values were determined. Overall the DES modification resulted in the highest chemical uptake with all methods. All the modifications also caused discoloration and darkening of the veneer material.

Distribution of chemicals within the 30% impregnated sample veneers was determined with SEM-EDX compound analysis. In DAP modified samples, most of the chemical was accumulated to the veneer surface or deposited in the pits. DES modification resulted in full chemical penetration throughout the veneer, which was also reflected by the high WPG values. Fixation of chemicals to the veneer in soaking and impregnation treatments was assessed according to the EN 84 standard. It was found that nearly all of the chemicals were completely leached out of the samples by the end of testing. Only a few SS treatments showed some resistance against leaching, but nevertheless the very small chemical content after leaching would be unlikely to have an effect on the fire resistance of the wood material.

Thermal properties and combustibility of modified veneers were analyzed with TGA and a simple fire resistance test. The results from the two tests supported each other. DAP proved to have superior fire resistance and TGA it shifted the pyrolysis pathway of wood to lower temperatures, which is an indicator of increased fire resistance. In actual fire resistance testing, DAP visibly promoted the char formation of the veneers. SS also performed relatively well. In fire resistance testing, it was noted that with samples of high WPG values good fire resistance could be achieved. In TGA testing DES had a strong effect on the wood pyrolysis in low temperatures, but less in high

temperatures, which in fire resistance testing translated to a slight fire resistance effect.

Wettability of impregnated veneers was analyzed by measuring contact angles by the sessile drop method. All the modifications lowered the contact angle values compared to the reference, which was to be expected with SS and DAP modifications, as they were known to increase the moisture content and therefore the hygroscopicity of wood. DES also lowered the contact angle. Glue bond strength of impregnated veneers was determined by ABES, where the glue bond strength of DAP modified samples exceeded that of reference. Despite their different chemical nature, SS and DES behaved similarly with each other and decreased the glue bond strength with short press times, which should be investigated further.

Overall the adhesion and wettability characteristics of fire retardant modified veneer remain poorly known, which leaves room for further research. More work should also be done in producing more leach-resistant systems. This does not necessarily involve the development of new chemicals, but rather taking advantage of the knowledge about already existing fire retardant chemicals and the processes that take place in wood in elevated temperatures. New pre-treatment methods based on the synergism of the two processes could be elaborated for a better fixation of chemicals in wood. Additionally, the potential of DES as a wood modification agent should be investigated further. It had an effect on the wettability of veneers, so it is likely to influence the important moisture properties of wood as well and overall the ways through which it interacts with the wood components should be understood better. The slight fire resistance effect could also be investigated further and the exact mechanism behind it should be determined.

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**APPENDIX 1.** Leaching test results

**Table 2.** Average leaching test results

| Treatment | WPG (%) | LEACHANT (%) | SD (Leachant) | Difference (WPG-Leachant) |
|---|---|---|---|---|
| Reference | 0 | 2,459260651 | 0,211169164 | |
| SS 30% imp. | 12,98425052 | 8,891669392 | 0,897736424 | 4,09258113 |
| DAP 30% imp. | 17,60759388 | 18,66018873 | 0,893023059 | -1,052594847 |
| DES 30% imp. | 16,60331154 | 13,34282856 | 1,172116499 | 3,260482977 |
| SS 15% imp. | 5,358508567 | 7,043867203 | 0,835543757 | -1,685358635 |
| DAP 15% imp. | 7,579613394 | 7,547266445 | 0,781530108 | 0,032346949 |
| DES 15% imp. | 9,490895424 | 10,14279924 | 0,888550165 | -0,651903818 |
| SS 30% 24 h | 9,18420243 | 8,277805743 | 0,747362045 | 0,906396687 |
| DAP 30% 24 h | 9,858466987 | 7,988330222 | 0,723852161 | 1,870136765 |
| DES 30% 24 h | 21,10152515 | 20,89826421 | 2,086031429 | 0,203260935 |
| SS 30% 3 h | 9,334570947 | 6,720114415 | 0,442608421 | 2,614456531 |
| DAP 30% 3 h | 6,593433521 | 8,73484367 | 1,096961059 | -2,141410149 |
| DES 30% 3 h | 16,10357893 | 14,80473779 | 0,646088603 | 1,298841137 |
| SS 15% 24 h | 4,809407659 | 4,983772986 | 0,46228223 | -0,174365327 |
| DAP 15% 24 h | 4,80581447 | 4,133066628 | 0,417453013 | 0,672747842 |
| DES 15% 24 h | 13,05390659 | 13,25010037 | 1,93956597 | -0,196193776 |
| SS 15% 3 h | 3,876148287 | 5,198059613 | 0,684644787 | -1,321911326 |
| DAP 15% 3 h | 2,679744225 | 4,06131641 | 0,529412957 | -1,381572185 |
| DES 15% 3 h | 6,433096685 | 6,754148874 | 0,498908838 | -0,321052189 |

**APPENDIX 2.** TGA graphs of pure chemicals

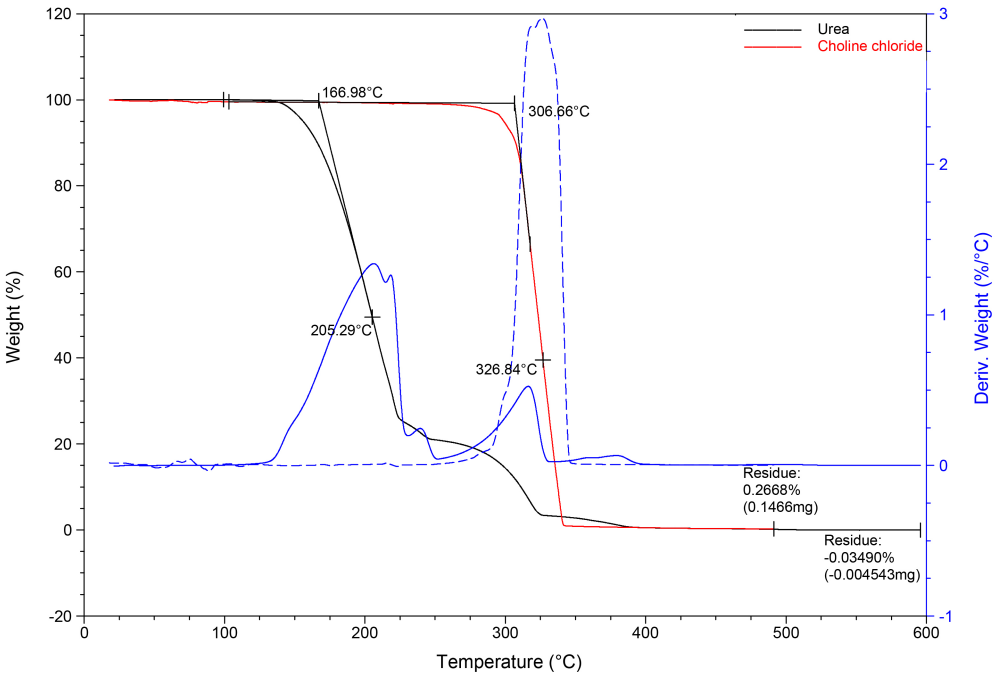


**Figure 25.** TGA and DTG graphs from the testing of pure choline chloride and urea.

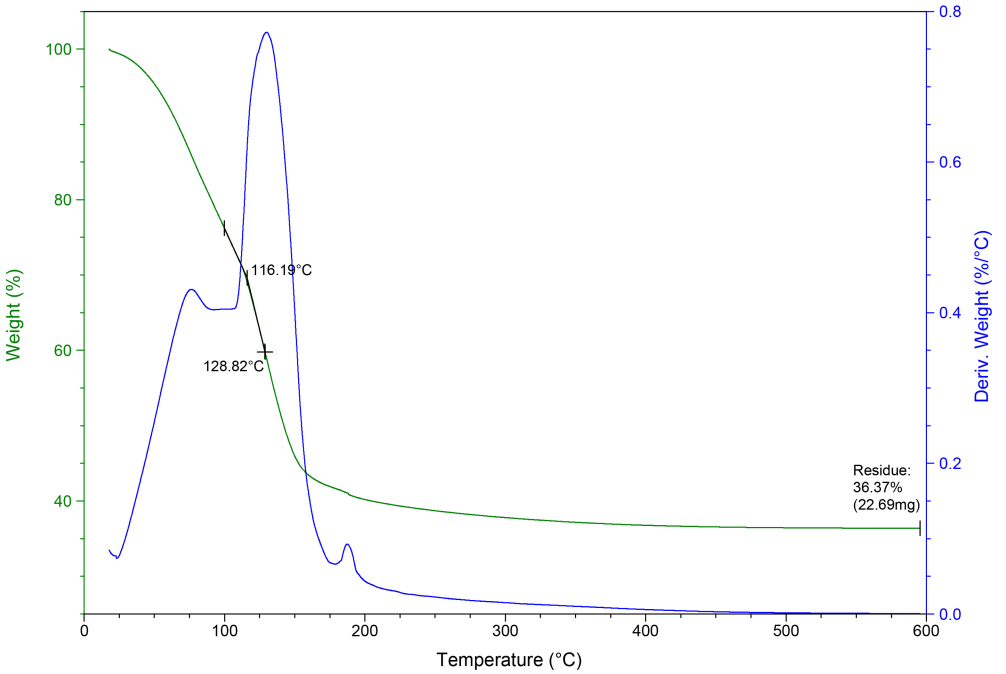


**Figure 26.** TGA and DTG graphs from the testing of pure SS.

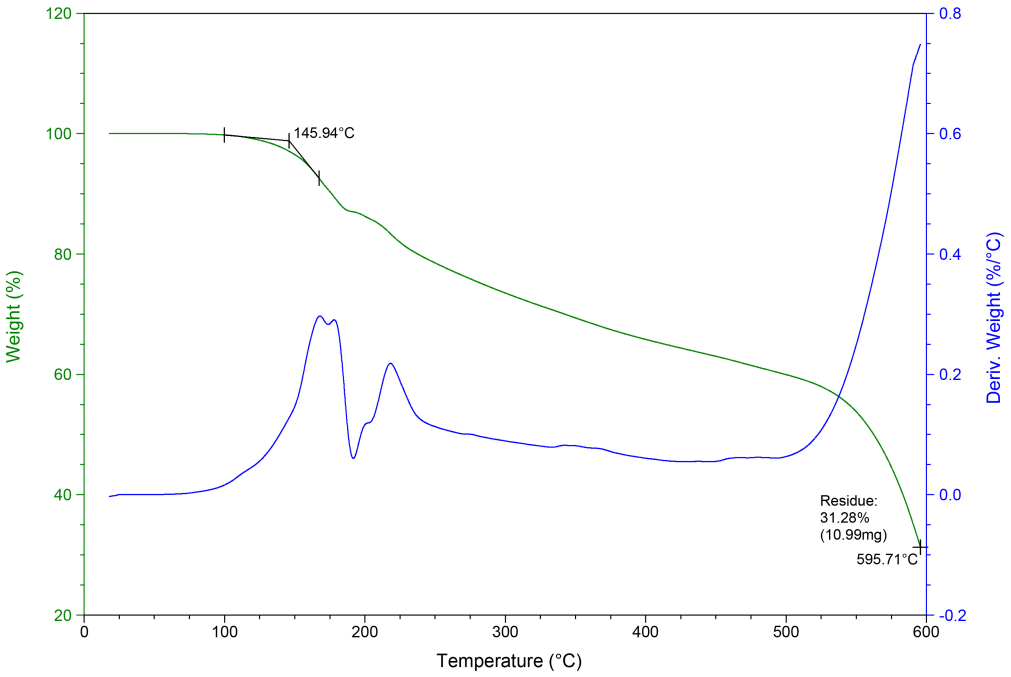


**Figure 27.** TGA and DTG graphs from the testing of pure DAP.

**APPENDIX 3.** TGA results

**Table 3.** TGA results

| Treatment | $T_{onset}$ | $T_{max}$ | RM |
|---|---|---|---|
| **Reference** | **257,37** | **362,23** | **13,09** |
| SS pure (aq) | 116,19 | 128,82 | 36,37 |
| SS 30% imp. | 256,79 | 304,75 | 33,51 |
| SS 15% imp. | 261,5 | 308,25 | 27,27 |
| SS 30% 24h | 248,67 | 293,75 | 22,78 |
| SS 30% 3h | 246,79 | 294,25 | 22,71 |
| SS 15% 24h | 262,93 | 306,85 | 30,67 |
| SS 15% 3h | 256,69 | 303,75 | 22,64 |
| Average | 255,5616667 | 301,9333333 | 26,59666667 |
| DAP pure | 145,94 | 600 | 31,28 |
| DAP 30% imp. | 237,53 | 278,26 | 30,45 |
| DAP 15% imp. | 200,76 | 274,26 | 30,38 |
| DAP 30% 24h | 228,54 | 273,12 | 40,09 |
| DAP 30% 3h | 248,58 | 287,75 | 28,2 |
| DAP 15% 24h | 211,56 | 281,26 | 24,79 |
| DAP 15% 3h | 248,05 | 286,26 | 26,86 |
| Average | 229,17 | 280,1516667 | 30,12833333 |
| CC pure | 306,66 | 326,84 | 0,26 |
| urea pure | 166,98 | 205,29 | 0 |
| DES 30% imp. | 159,35 | 358,73 | 12,65 |
| DES 15% imp. | 159,11 | 363,72 | 12,33 |
| DES 30% 24h | 165,39 | 352,73 | 14,47 |
| DES 30% 3h | 160,31 | 351,23 | 11,43 |
| DES 15% 24h | 162,56 | 351,76 | 12,11 |
| DES 15% 3h | 160,62 | 345,7 | 6,056 |
| Average | 161,2233333 | 353,9783333 | 11,50766667 |

**APPENDIX 4.** Average ABES results

**Table 4**. Average ABES results

| Press time (s) | Glue bond strength (Mpa) | |
|---|---|---|
| | Reference | SD (Ref) |
| 60 | 359,7857143 | 44,34097272 |
| 100 | 419,19 | 83,75050408 |
| 140 | 415,5385714 | 61,22285832 |
| 180 | 387,0216667 | 86,8564009 |
| | SS 30% imp. | SD (SS 30% imp.) |
| 60 | 275,7733333 | 23,17421316 |
| 100 | 316,3333333 | 40,11606647 |
| 140 | 386,4133333 | 45,49031899 |
| 180 | 418,29 | 34,19850679 |
| | DAP 30% imp. | SD (DAP 30% imp.) |
| 60 | 573,5366667 | 30,87266194 |
| 100 | 609,915 | 65,61173237 |
| 140 | 684,3228571 | 106,5213104 |
| 180 | 742,13625 | 100,4532371 |
| | DES 30% imp. | SD (DES 30% imp.) |
| 60 | 252,7016667 | 41,36040394 |
| 100 | 307,0171429 | 37,89347389 |
| 140 | 385,6833333 | 29,6127769 |
| 180 | 411,355 | 20,54294019 |
| | SS 15% imp. | SD (SS 15% imp.) |
| 60 | 334,2471429 | 40,2160056 |
| 100 | 417,4728571 | 84,97310141 |
| 140 | 425,8642857 | 57,84739255 |
| 180 | 477,65 | 85,92271605 |
| | DAP 15% imp. | SD (DAP15% imp.) |
| 60 | 600,4216667 | 79,9798736 |
| 100 | 580,9666667 | 111,0427366 |
| 140 | 664,4216667 | 126,4758211 |
| 180 | 668,4366667 | 92,26313125 |
| | DES 15% imp. | SD (DES 15% imp.) |
| 60 | 304,68375 | 51,09600766 |
| 100 | 391,8883333 | 34,79177413 |
| 140 | 432,2816667 | 48,86715578 |
| 180 | 465,1316667 | 27,74133403 |